Kinetic Theory of Gases & Thermodynamics

for

M.Sc. Entrance

IIT-JAM | JNU | TIFR | JEST | BHU | ISM | JNCASR | DU

First Edition	:	November 2015
Second Edition	:	July 2017

CAREER ENDEAVOUR PUBLICATIONS has taken due care in collecting the data and providing the solutions, before publishing this book. Inspite of this, if any inaccuracy or printing errors are there, **CAREER ENDEAVOUR PUBLICATIONS** owes no responsibility. **CAREER ENDEAVOUR PUBLICATIONS** will be grateful if you could point out any such error. Your suggestions will be highly appreciated.

© **All right reserved by CAREER ENDEAVOUR PUBLICATIONS**. No part of this book may be reproduced or utilized in any form without the written permission from the publisher.

CAREER ENDEAVOUR Publications

Regd. Office: 28-A/11, Jia Sarai, New Delhi-16, **Ph:** 011-26851008, 26861009
E: info@careerendeavour.in, **W:** www.careerendeavour.in

TABLE OF CONTENTS

CHAPTER 01: KINETIC THEORY OF GASES **01-21**

- Postulates of Kinetic Theory 01
- Pressure Exerted by a Gas 02
- Molecular Speeds Distribution 07
- The Maxwell-Boltzmann Distribution 07
- Degree of Freedom 14
- Law of Equipartition of Energy 15
- Mean Free Path 18
- Problems to be Played 20

CHAPTER 02: THE GAS LAWS & THE FIRST LAW OF THERMODYNAMICS **22-52**

- The Gas Laws 22
- Different Types of Temperature in Thermodynamics 28
- Terms in Thermodynamics 29
- Types of Walls 30
- Zeroth Law of Thermodynamics 31
- Internal Energy 31
- Work 31
- Heat 32
- Sign Convention 33
- First Law of Thermodynamics 33
- Application of First Law of Thermodynamics 36
- Bulk Modulus or Incompressibility 47
- Isothermal Compressibility 47
- Coefficient of Volume Expansion 47
- Problems to be played 49

CHAPTER 03: THE CARNOT ENGINE **53-64**

- The Carnot Engine 53
- The Heat Engine 55
- Refrigerator and Heat Pump 59
- Negative Temperature 60
- Carnot Theorem 61
- Problems to be Played 63

Chapter 04: THE ENTROPY & THE SECOND LAW OF THERMODYNAMICS **65-82**

- Entropy 65
- Change in Entropy in Some Processes 67
- Change in Entropy in Conversion Processes 72
- Change in Entropy in Terms of Different Parameters 74
- Temperature-Entropy Diagram 76
- The Second Law of Thermodynamics 78
- The Third Law of Thermodynamics 78
- Problems to be Played 79

CHAPTER 05: THERMODYNAMICS POTENTIALS & MAXWELL RELATIONS **81-96**

- Thermodynamic Potentials 81
- Maxwell Equations 87
- Problems to be Played 95

CHAPTER 06 : THE PHASE TRANSITION **97-105**

- Clausius Clapeyron Equation 97
- Phase Transition 99
- Triple Point 103
- Problems to be Played 105

CHAPTER 07: STATISTICAL MECHANICS **106-135**

- Fundamental Concepts and Theorems 106
- Micro-canonical Ensemble 111
- The Canonical Ensemble 114
- Classical and Quantum Statistics 126
- Problems to be Played 134

APPENDIX-I: SPECIFIC & LATENT HEATS **136**

APPENDIX-II: THERMAL EXPANSION **137**

APPENDIX-III: THERMAL CONDUCTION **140**

APPENDIX-IV: BLACKBODY RADIATION **142**

APPENDIX-V: JOULE THOMSON EXPERIMENT **144**

Chapter 1

Kinetic Theory of Gases

Postulates of Kinetic Theory

Suppose a container with volume V contains a very large number N of identical molecules, each with mass m. Then, the kinetic theory postulates the following

(1) The molecules behave as point particles that are small compared to the size of the container and to the average distance between molecules.

(2) The molecules are in constant motion. Each molecule collides occasionally with a wall of the container. These collisions are perfectly elastic.

(3) There is no force of attraction among the gas molecules and between the gas molecules and walls of the container.

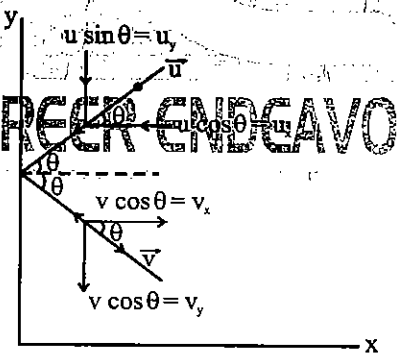
(4) The container walls are rigid and infinitely massive and do not move.

(5) The molecules obey Newton's law of motion.

(6) The time of collision is much less than the averaged time between two successive collision.

Meaning of elastic collision

If a molecule with velocity $\vec{u}$ strikes a wall align along y-axis, then the collision is *elastic* if



CAREER ENDEAVOUR

- Velocity component parallel to wall (y-component) does not change, i.e., $v_y = u_y$.
- Velocity component perpendicular to wall (x-component) reverses direction, i.e., $v_x = -u_x$.
- Speed v does not change, i.e., $|\vec{v}| = |\vec{u}|$.

Note : We will follow these notations throughout the book.

N = Number of molecules in the gas

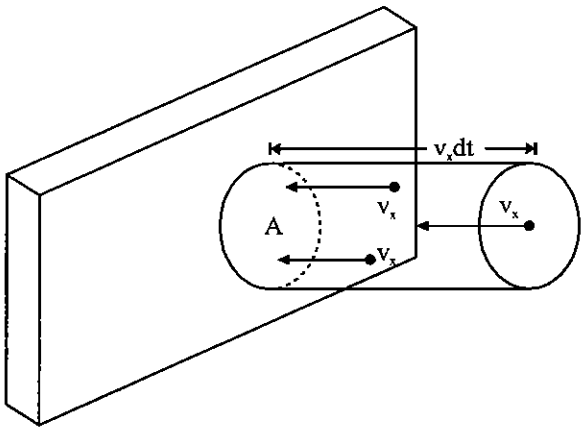
n = Number of moles in the gas

N_A = Avagadro number

where $\boxed{N = nN_A}$

Pressure Exerted by a Gas

During collisions, the molecules exert forces on the walls of the container, this is the origin of the pressure that the gas exerts on the wall of the container.



Steps to calculate the pressure exerted by gas molecules on the walls of the container

1. Number of collisions that occur per unit time for a certain area A of the wall.
2. Total momentum associated with these collisions
3. Force needed to cause this momentum change.

Assuming that all molecules in the gas have the same magnitude of x-velocity, $|v_x|$.

For each collision the x-component of velocity changes from $-|v_x|$ to $|v_x|$

So, the change in the momentum is $\Delta p_x = m|v_x| - (-m|v_x|) = 2m|v_x|$ ... (1)

If a molecule is going to collide with a given wall area A during a small time interval dt, then at the beginning of time dt if must be within a distance $|v_x|\,dt$ from the wall and it must be headed toward the wall.

$\Rightarrow$ Total number of molecules that collide with area A during time interval dt $\equiv$ Number of molecules with base area A and length $|v_x|\,dt$ and leading towards the wall.

CAREER ENDEAVOUR

where volume of cylinder = $A|v_x|\,dt$

Assuming uniform distribution of molecules, number of molecules in this cylinder = $\left(\frac{N}{V}\right)\left(A|v_x|\,dt\right)$

On the average, half of these molecules are moving towards the wall (that causes pressure) and half are moving away from it.

$\Rightarrow$ Number of collision with A during dt = $\frac{1}{2}\left(\frac{N}{V}\right)\left(A|v_x|\,dt\right)$ ... (2)

Due to all molecules in the gas, the total momentum change during dt is

$$dp_x = (\text{No. of collisions}) \times 2m|v_x|$$

$$= \frac{1}{2}\left(\frac{N}{V}\right)\left(A|v_x|\,dt\right) \times 2m|v_x|$$

$$= \frac{NAm}{V} v_x^2\,dt \qquad \left[\because |v_x|^2 = v_x^2\right]$$

$$\Rightarrow \frac{dp_x}{dt} = \frac{NAm\,v_x^2}{V} \quad \ldots (3)$$

According to Newton's second law, this rate of change of momentum equals the force exerted by the wall area A on the gas molecules. From Newton's III law, this is equal and opposite to the force exerted on the wall by the molecules.

So pressure P is the magnitude of the force exerted on the wall per unit area is

$$P = \frac{F}{A} = A\frac{dp_x}{dt} = \left(\frac{N}{V}\right)mv_x^2 \quad \ldots (4)$$

$\Rightarrow$ Pressure exerted by the gas depends on the number of molecules per unit volume (N/V), the mass m per molecule, and the speed of the molecules.

Note: $|v_x|$ is really not the same for all the molecules. But we could have sorted the molecules into groups having the same $|v_x|$ with each group, where net effect of the molecules is $\left(v_x^2\right)$avg.

Also, speed v of 'a' molecules is $v^2 = v_x^2 + v_y^2 + v_z^2$

For all molecules.

$$\left(v^2\right)_{avg} = \left(v_x^2\right)_{avg} + \left(v_y^2\right)_{avg} + \left(v_z^2\right)_{avg} \quad \ldots (5)$$

Since there is no real difference in our model between $x-$, $y-$ and $z-$ direction,

$$\langle v_x^2\rangle_{avg} = \left(v_y^2\right)_{avg} = \left(v_z^2\right)_{avg}$$

$$\therefore \quad \langle v^2\rangle_{avg} = 3\langle v_x^2\rangle_{avg}$$

$$\Rightarrow \quad \left(v_x^2\right)_{avg} = \frac{1}{3}\left(v^2\right)_{avg} \quad \ldots (6)$$

Using (4), we have

$$P = \frac{1}{3}\frac{N}{V}m\left(v^2\right)_{avg}$$

$$\Rightarrow \quad PV = \frac{1}{3}Nm\left(v^2\right)_{avg} \quad \left[\because \left(v^2\right)_{avg} = \left(\overline{v}^2\right) = \langle v^2\rangle\right] \quad \ldots (7)$$

CAREER ENDEAVOUR

Now the average translational Kinetic energy (KE) of a single molecule $= \frac{1}{2}m\left(v^2\right)_{avg}$.

So the total random kinetic energy K_{tr} of translational motion of all the molecules is

$$K_{tr} = \frac{N}{2}m\left(v^2\right)_{avg} \quad \ldots (8)$$

(There may be other energies also associated with rotation and vibration of molecules but we are considering only translational energy)

Equations (7) and (8) $\Rightarrow$ $\boxed{PV = \frac{2}{3}K_{tr.}}$ ... (9)

Comparing will ideal gas equation

$$PV = nRT$$

which is based on experimental studies of gas behavior, we have

$$\boxed{K_{tr} = \frac{3}{2}nRT}\ ;\ T = \text{ absolute temperature} \quad \ldots (10)$$

This is average translational kinetic energy of 'n' moles of ideal gas which clearly shows that translational kinetic energy depends only on the temperature of the gas.

Now, average translational kinetic energy of 'a' single molecule

$$= \frac{K_{tr.}}{N} = \frac{3\,nRT}{2\,N} \qquad \ldots (11)$$

where $n = nN_A$ $\ldots (12)$

So, $\frac{K_{tr}}{N} = \frac{3}{2}\left(\frac{R}{N_A}\right)T$ $\ldots (13)$

The ratio $\frac{R}{N_A}$ occurs requently in molecular theory. It is called Boltzmann's constant k_B.

$$\Rightarrow \quad k_B = \frac{R}{N_A} = \frac{8.314 \text{ J/mol}\cdot\text{K}}{6.022\times10^{23} \text{ molecules/mol}} = 1.381\times10^{-23} \text{ J/molecules}\cdot\text{K}$$

So, average kinetic translational energy of a molecule $= \frac{3}{2}k_BT$

Molecular Speeds

The average translational kinetic energy is equals to $\frac{3}{2}k_BT$. Also, from the basic definition of kinetic energy, the average translational kinetic energy must also be equals to $\frac{1}{2}m\left(v^2\right)_{avg.}$ So,

$$\frac{1}{2}m\left(v^2\right)_{avg.} = \frac{3}{2}k_BT$$

where square-root of $\left(v^2\right)_{avg}$ = Root-mean square speed (or rms speed) v_{rms}

CAREER ENDEAVOUR

$$\therefore \quad v_{rms} = \sqrt{\left(v^2\right)_{avg}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}} \qquad \left[\because k_B = \frac{R}{N_A}\right]$$

where, M is the molar mass of the gas and is equal to mN_A.

Problem: Why there is hardly any hydrogen gas (H_2) in the earth's atmosphere, despite its being the most common element in the universe ?

Soln. Molar mass of hydrogen gas, $M = 2\times10^{-3}$ kg

$$\therefore \quad v_{\text{r.m.s.}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times8.314\times300}{2\times10^{-3}}} \qquad [\because T = 300 \text{ K (room temperature)}]$$

$$= 1.934 \text{ km/sec}$$

A sizeable fraction of H_2 molecule in the atmosphere would have speeds greater than the earth's escape of 11.2 km/sec.

On the other hand, the heavier, slowly moving gases, can't escape so easily which is why they predominate in our atmosphere.

Problem: At room temperature, the rms speed of the molecules of a certain diatomic gas is found to be 1930 m/s. The gas is

(a) H_2 (b) F_2 (c) O_2 (d) Cl_2

[IIT-JEE : 1984]

Soln. $v_{rms} = \sqrt{\frac{3RT}{M}}$

Room temperature $T \approx 300\ K$

$\therefore \quad 1930 = \sqrt{\frac{3 \times 8.31 \times 10^3 \times 300}{M}}$

$\therefore \quad M = 2.0$ g/mol or the gas is H_2.

Correct option is (a)

Problem: What is the average translational kinetic energy of a molecule in 1 mole of a gas at 27°C ?

(a) 6.21 x 10^{-21} J (b) 6.21 x 10^{-22}J (c) 6.21 x 10^{-23}J (d) 6.21 x 10^{-20}J

Soln. Given : $T = 27\,^\circ C = 300$ K

Avgerage K_{tr} per molecule $= \frac{3}{2} k_B T = \frac{3}{2} \times 1.381 \times 10^{-23} \times 300 = 6.21 \times 10^{-21}$ J

Correct option is (a)

Problem: Five gas molecules chosen at random are found to have speeds of 500, 600, 700, 800 and 900 m/s? What is the rms speed and average speed?

(a) v_{rms}=700 m/s and v_{av}= 714 m/s (b) v_{rms}=71.4 m/s and v_{av}= 70.4 m/s

(c) v_{rms}=714 m/s and v_{av} = 700 m/s (d) v_{rms}=70.4 m/s and v_{av}= 71.4 m/s

Soln. Given : $v_1 = 500$ m/s, $v_2 = 600$ m/s, $v_3 = 700$ m/s, $v_4 = 800$ m/s, $v_5 = 900$ m/s

$$v_{avg.} = \frac{\sum_{i=1}^{5} v_i}{5} = \frac{500 + 600 + 700 + 800 + 900}{5} = 700 \text{ m/s}$$

CAREER ENDEAVOUR

$$\text{and } v_{r.m.s.} = \left(\frac{\sum_{i=1}^{5} v_i^2}{5} \right)^{1/2} = \left(\frac{500^2 + 600^2 + 700^2 + 800^2 + 900^2}{5} \right)^{1/2} = 714.14 \text{ m/s}$$

Correct option is (c)

Problem: Assuming that the hydrogen molecules have a root-mean-square speed of 1270 m/s at 300 K, calculate the rms at 600 K.

(a) 179.6 m/s (b) 1796 m/s (c) 2796 m/s (d) 279.6 m/s

Soln. Given : $(v_{r.m.s.})_1 = 1270$ m/s, $T_1 = 300$ K and $(v_{r.m.s.})_2 = ?$, $T_2 = 600$ K

Since, $(v_{r.m.s.}) = \sqrt{\frac{3 k_B T}{m}} \Rightarrow \frac{(v_{r.m.s.})_1}{(v_{r.m.s.})_2} = \sqrt{\frac{T_1}{T_2}}$

$$\Rightarrow (v_{r.m.s.})_2 = \sqrt{\frac{T_2}{T_1}}\,(v_{r.m.s.})_1 = \sqrt{2} \times 1270 = 1796 \text{ m/s}.$$

Correct option is (b)

Problem: One gram mole of oxygen at 27°C and one atmospheric pressure is enclosed in a vessel.

(a) Assuming the molecules to be moving with v_{rms}, find the number of collisions per second which the molecules make with one sqaure metre area of the vessel wall.

(b) The vessel is next thermally insulated and moved with a constant speed v_0. It is then suddenly stopped. The process results in a rise of the temperature of the gas by 1°C. Calculate the speed v_0. **[IIT-JEE : 1983]**

Soln. **(a)** $v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 300}{32 \times 10^{-3}}} = 483.4 \text{ m/s}$

Given, $P_0 = 1.01 \times 10^5$ N/m^2 = Force per unit area. Let n molecules of oxygen strike the wall per second per m^2 and recoil with same speed.

Change in momentum is $(2nmv_{rms})$.

The change in momentum per unit time is the force.

Hence, $P_0 = 2nmv_{rms}$

$$\therefore \quad n = \frac{P_0}{2mv_{rms}} = \frac{1.01 \times 10^5}{2\left[\frac{32}{6.02 \times 10^{26}}\right](483.4)} = 1.96 \times 10^{27}/\text{s}$$

(b) $\frac{1}{2}(m_{gas})v_0^2 = nC_V\Delta T$

$$\therefore \quad v_0 = \sqrt{\frac{2nC_V\Delta T}{m_{gas}}} = \sqrt{\frac{(2)\,(n)\left(\frac{5}{2} \times 8.31\right)(1)}{(n)\,(32 \times 10^{-3})}} = 36 \text{ m/s}$$

Problem: A cubical box of side 1 m contains helium gas (atomic weight 4) at a pressure of 100 N/m^2. During an observation time of 1 s, an atom travelling with the root mean square speed parallel to one of the edges of the cube, was found to make 500 hits with a particular wall, without any collision with other atoms. Take, $R = \frac{25}{3}$ J/mol-K and $k_B = 1.38 \times 10^{-23}$ J/K. **[IIT-JEE : 2002]**

(a) Evaluate the temperature of the gas.

(b) Evaluate the average kinetic energy per atom.

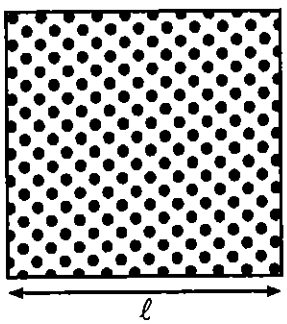
(c) Evaluate the total mass of helium gas in the box.

Soln. Volume of the box = 1 m^3

Pressure of the gas = 100 N/m^2

Let T be the temperature of the gas. Then,

(a) Time between two consecutive collisions with one wall = $\frac{1}{500}$ s. This time should be equal to $\frac{2l}{v_{rms}}$, where l is the side of the cube.



$$\Rightarrow \quad \frac{2l}{v_{rms}} = \frac{1}{500}$$

$$\Rightarrow \quad v_{rms} = 1000 \text{ m/s} \quad (\text{as } l = 1 \text{ m})$$

$$\Rightarrow \quad \sqrt{\frac{3RT}{M}} = 1000$$

$$\therefore \quad T = \frac{(1000)^2 M}{3R} = \frac{(10)^6 (4 \times 10^{-3})}{3(25/3)} = 160 \text{ K}$$

(b) Average kinetic energy per atom $= \frac{3}{2} k_B T = \frac{3}{2} (1.38 \times 10^{-23}) (160) \text{ J} = 3.312 \times 10^{-21} \text{ J}$

(c) From $PV = nRT = \frac{m}{M} RT$

We get mass of helium gas in the box, $m = \frac{PVM}{RT}$

Substituting the values, we get

$$m = \frac{(100)(1)(4)}{(25/3)(160)} = 0.3 \text{ g}$$

Molecular Speeds Distribution

The molecules in a gas don't have the same speed. We will study a function $f(v)$ that will help us to know how a particular number of molecules possess a certain amount of speed. This function is called distribution function.

If we observe total N molecules, the number dN having speeds in the range between v and $v + dv$ is given by

$$dN = N f(v) dv \qquad \ldots (17)$$

Probability that a random chosen molecule will have a speed in the interval v to $v + dv$ is

$$f(v) dv \qquad \ldots (18)$$

CAREER ENDEAVOUR

Hence $f(v)$ is the probability per unit speed interval.

It is not equal to the probability that a molecule has speed exactly equals to v.

Since probability is pure number, $f(v)$ has units of reciprocal speed (s/m).

The Maxwell-Boltzmann Distribution

The function $f(v)$ describing the actual distribution of molecular speeds is called the *Maxwell-Boltzmann distribution.*

Deriving from the statistical mechanics. it is equal to

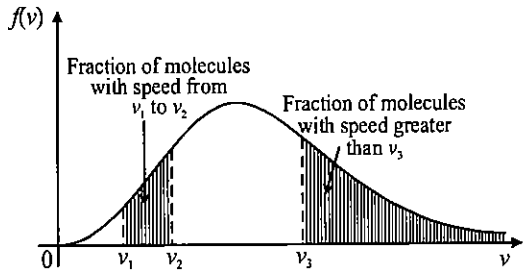
$$\boxed{f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}}, \quad 0 \le v < \infty \qquad \ldots (19)$$

where m is the mass of a molecule

v is the velocity, different for different group of molecules.

T is the absolute temperature.

The graph representing Maxwell-Boltzmann distribution is



Each molecule must have some value of v, so the integral of $f(v)$ over all v must be unity for any T i.e.

$$\int_0^\infty f(v)dv = 1$$

At each temperature, the height of the curve for any value v is proportional to the number of molecules with speeds near v.

The various speeds possess by molecules:

(1) The average speed (v_{av})

It is the average speed possesses by the molecules of the gas.

It is given by

$$v_{av} = \int_0^\infty v f(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}}dv$$

Using $\int_0^\infty x^n e^{-ax^2}dx = \frac{\Gamma\left(\frac{n+1}{2}\right)}{2a^{\frac{n+1}{2}}}$, we have ... (20)

$$v_{av} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\frac{\Gamma 2}{2\left(\frac{m}{2k_B T}\right)^2} = \frac{4\pi}{\pi^{3/2}}\left(\frac{m}{2k_B T}\right)^{-\frac{1}{2}}\frac{1}{2} = \sqrt{\frac{8k_B T}{\pi m}} \quad ... (21)$$

CAREER ENDEAVOUR

$$\boxed{v_{av} = \sqrt{\frac{8k_B T}{\pi m}}}$$

where $\Gamma n = (n-1)!$ if n is an integer.

(2) Most probable speed (v_{mp})

It is the speed possesses by the maximum number of molecules. For this speed, the value of $f(v)$ is maximum. So using (19) and concept of maxima and minima, we have $\frac{d}{dv}f(v) = 0$

$$\Rightarrow 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left[2ve^{-\frac{mv^2}{2k_B T}} - \frac{2mv^3}{2k_B T}e^{-\frac{mv^2}{2k_B T}}\right] = 0$$

$$\Rightarrow 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} 2ve^{-\frac{mv^2}{2k_B T}}\left[1 - \frac{mv^2}{2k_B T}\right] = 0$$. This gives

Either $v = 0$

or, $e^{-\frac{mv^2}{2k_BT}} = 0 \Rightarrow v = \infty$

or, $1 - \frac{mv^2}{2k_BT} = 0 \Rightarrow v = \sqrt{\frac{2k_BT}{m}}$

The speeds of the molecule can neither be zero nor infinite (as per as the assumption of the kinetic theory as the molecules are in constant motion with finite speed).

So $\boxed{v_{mp} = \sqrt{\frac{2k_BT}{m}}}$ ... (22)

(3) The rms speed (v_{rms})

It is the speed observed during the experiments and is given by

$$v_{rms} = \sqrt{\overline{v}^2} \quad \text{... (23)}$$

Now $\overline{v}^2 = \int_0^\infty v^2 f(v)dv = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} \int_0^\infty v^4 e^{-\frac{mv^2}{2k_BT}} dv$

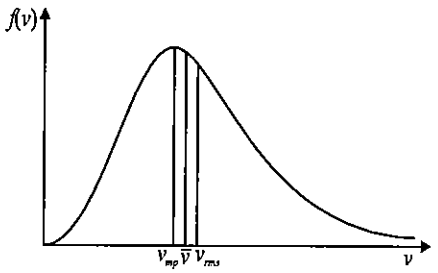
Using $\int_0^\infty x^n e^{-ax^2} dx = \frac{\boxed{\frac{n+1}{2}}}{2a^{\frac{n+1}{2}}}$

$\therefore \quad \overline{v}^2 = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} \frac{\boxed{5/2}}{2\left(\frac{m}{2k_BT}\right)^{5/2}} = \frac{3k_BT}{m}$

So $\boxed{v_{rms} = \sqrt{\overline{v}^2} = \sqrt{\frac{3k_BT}{m}}}$ ... (24)

CAREER ENDEAVOUR

The graph representing v_{rms}, $\overline{v}_{avg}$, v_{mp} is



Problem: A quantity of gas containing N molecules has a speed distribution function $f(v)$. How many molecules have speeds between v_1 and $v_2 > v_1$?

(a) $\int_0^{v_2} f(v)dv - \int_0^{v_1} f(v)dv$ (b) $N\left[\int_0^{v_2} f(v)dv - \int_0^{v_1} f(v)dv\right]$

(c) $\int_0^{v_1} f(v)dv - \int_0^{v_2} f(v)dv$ (d) $n\left[\int_0^{v_1} f(v)dv - \int_0^{v_2} f(v)dv\right]$

Soln. Required number $= \int_{v_1}^{v_2} N f(v)\,dv = N\left[\int_0^{v_2} f(v)dv - \int_0^{v_1} f(v)dv\right]$

Correct option is (b)

Problem: Which of the inequality is valid for molecular distribution of gas?

(a) $v_{rms} > \overline{v} > v_{m.p.}$ (b) $v_{rms} > v_{m.p.} > \overline{v}$ (c) $v_{m.p.} > \overline{v}_{rms} > \overline{v}$ (d) $v_{m.p.} > \overline{v} > v_{rms}$

Soln. We know that, $v_{\text{r.m.s.}} = \sqrt{\frac{3RT}{M}}$; $v_{\text{m.p.}} = \sqrt{\frac{2RT}{M}}$; $v_{\text{avg.}} = \overline{v} = \sqrt{\frac{8RT}{\pi M}}$

Clearly, $v_{\text{r.m.s.}} : v_{\text{m.p.}} : \overline{v} = \sqrt{3} : \sqrt{2} : \sqrt{\frac{8}{\pi}}$

$= 1.732 : 1.414 : 1.596$

$\Rightarrow v_{\text{r.m.s.}} : \overline{v} : v_{\text{m.p.}} = 1.732 : 1.596 : 1.414$

So, $v_{\text{r.m.s.}} > \overline{v} > v_{\text{m.p.}}$

Correct option is (a)

Another forms of Maxwellian distribution

It is given by

$$f(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} dv \qquad \ldots (25)$$

(1) Energy form

Since $\varepsilon = \frac{1}{2}mv^2 \Rightarrow v^2 = \frac{2\varepsilon}{m}$

Using this in equation (25),

$$f(\varepsilon)d\varepsilon = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left(\frac{2\varepsilon}{m}\right)e^{-\varepsilon/k_B T}\left(\frac{d\varepsilon}{\sqrt{2\varepsilon m}}\right)$$

$$= 4\sqrt{2}\,\pi\left(\frac{1}{2\pi k_B T}\right)^{3/2}\sqrt{\varepsilon}\, e^{-\varepsilon/k_B T} d\varepsilon \qquad \ldots (26)$$

(2) Momentum form

Now, $p = mv$ or $v = \frac{p}{m}$

Using this in (25),

$$f(p)dp = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\frac{p^2}{m^3} e^{-\frac{1}{2k_B T}\frac{p^2}{m}} dp \qquad \ldots (27)$$

Maxwellian speed distribution in different dimensions

(i) In three dimension : $f(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}$

(ii) In two dimension : $f(v) = 2\pi\left(\frac{m}{2\pi k_B T}\right)^{2/2} v\, e^{-\frac{mv^2}{2k_B T}}$

(iii) In one dimension : $f(v) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_B T}}$

Problem : Three closed vessels A, B and C at the same temperature T and contain gases which obey the Maxwellian distribution of velocities. Vessels A contains only O_2, B only N_2 and C a mixture of equal quantities of O_2 and N_2. If the average speed of the O_2 molecules in vessel A is v_1, that of the N_2 molecules in vessel B is v_2, the average speed of the O_2 molecules in vessel C is **[IIT-JEE : 1992]**

(a) $(v_1 + v_2)/2$ (b) v_1 (c) $(v_1\, v_2)^{1/2}$ (d) $\sqrt{3k_B T/M}$

Soln. The average speed of molecules of an ideal gas is given by

$\langle v \rangle = \sqrt{\frac{8RT}{\pi M}}$ *i.e.*, $\langle v \rangle \propto \sqrt{T}$ for same gas.

Since temperature of A and C are same, average speed of O_2 molecules will be equal in A and C i.e., v_1.

So, the correct option is (b)

Problem: The temperature of an ideal gas is increased from 120 K to 480 K. If at 120 K at the root mean sqaure velocity of the gas molecules is v, at 480 K it becomes **[IIT-JEE : 1996]**

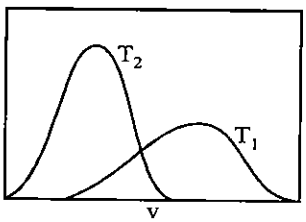
(a) 4 v (b) 2 v (c) v/2 (d) v/4

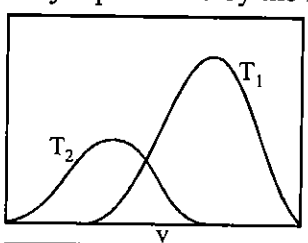
Soln. $v_{rms} = \sqrt{\frac{3RT}{M}}$ i.e., $v_{rms} \propto \sqrt{T}$

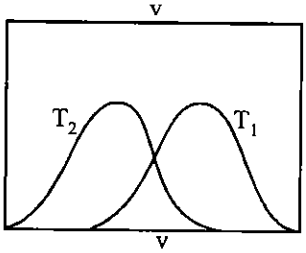
When temperature is increased from 120 K to 480 K (i.e., four times), the root mean square speed will becomes $\sqrt{4}$ or 2 times i.e., 2v.

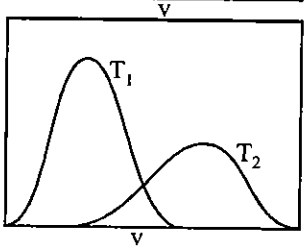
So, the correct option is (b)

Problem: For temperature $T_1 > T_2$, the qualitative temperature dependence of the probability distribution $F(v)$ of the speed v of a molecule in three dimensions is correctly represented by the following figure:

(a) 

(b) 

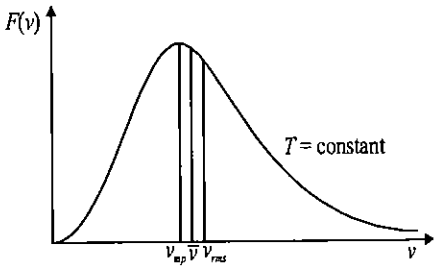
(c) 

(d) 

Soln. For N-particles system in thermal equilibrium, the number of molecules having speed between v to $v+dv$ is given by

$$F(v)dv = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 dv$$

$$\Rightarrow F(v) = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 \text{ and } \int_0^\infty F(v)dv = N$$



and $\bar{v} = \sqrt{\frac{8k_BT}{\pi m}}, v_p = \sqrt{\frac{2k_BT}{m}}, v_{rms} = \sqrt{\frac{3k_BT}{m}}$

If we increase temperature, then $\bar{v}$, $\bar{v}_p$ and v_{rms} all will increase and particles have more values of velocities. More particles will distribute in large velocity region but total number of particles in the system will be constant (N). In $F(v)$ Vs. v plot area under the curve remain constant. So on increasing the temperature, peak will decrease and shifted towards higher velocity side.

Correct answer is (a)

Problem: Let $\bar{v}$, $\bar{v}_p$ and v_{rms} respectively denote the mean speed, root mean square speed and most probable speed of the molecules in an ideal monoatomic gas at absolute temperature T. The mass of a molecule is m. Then,

(a) no molecule can have a speed greater than $\sqrt{2}\, v_{rms}$

(b) no molecule can have a speed less than $v_p/\sqrt{2}$

(c) $v_p < \bar{v} < v_{rms}$

(d) the average kinetic energy of a molecule is $\frac{3}{4}mv_p^2$

[IIT-JEE : 1998]

Soln. $v_{rms} = \sqrt{\frac{3RT}{M}}, \bar{v} = \sqrt{\frac{8}{\pi}\cdot\frac{RT}{M}} = \sqrt{\frac{2.5RT}{M}}$ and $v_p = \sqrt{\frac{2RT}{M}}$

From these expressions we can see that, $v_p < \bar{v} < v_{rms}$

Secondly, $v_{rms} = \sqrt{\frac{3}{2}}\, v_p$

and average kinetic energy of a gas molecule

$$= \frac{1}{2}mv_{rms}^2 = \frac{1}{2}m\left(\sqrt{\frac{3}{2}}\, v_p\right)^2 = \frac{3}{4}mv_p^2.$$

Hence, correct options are (c, d)

Problem: Consider a Maxwellian distribution of the velocity of the molecules of an ideal gas. Let v_{mp} and v_{rms} denote the most probable velocity and the root mean square velocity, respectively. The magnitude of the ratio v_{mp}/v_{rms} is:

(a) 1 (b) 2/3 (c) $\sqrt{2/3}$ (d) 3/2

Soln. $f(\mathrm{v}) \propto \mathrm{v}^2 \exp\left(-\frac{m\mathrm{v}^2}{2k_BT}\right) \Rightarrow \frac{df}{d\mathrm{v}} = 0 \Rightarrow \mathrm{v}_{mp} = \sqrt{\frac{2k_BT}{m}}$

and $\mathrm{v}_{rms} = \left[\int_0^\infty \mathrm{v}^2 f(\mathrm{v})\, d\mathrm{v}\right]^{1/2} = \sqrt{\frac{3k_BT}{m}}$

$\therefore \quad \frac{\mathrm{v}_{mp}}{\mathrm{v}_{rms}} = \sqrt{\frac{2}{3}}$

Correct answer is (c).

Problem: A gas of molecules each having mass m is in the thermal equilibrium at a temperature T. Let v_x, v_y, v_z be the Cartesian components of velocity $\bar{\mathrm{v}}$ of a molecule. The mean value of $(\mathrm{v}_x - \alpha \mathrm{v}_y + \beta \mathrm{v}_z)^2$ is

(a) $(1+\alpha^2+\beta^2)\frac{k_BT}{m}$ (b) $(1-\alpha^2+\beta)\frac{k_BT}{m}$

(c) $(\beta^2-\alpha^2)\frac{k_BT}{m}$ (d) $(\alpha^2+\beta^2)\frac{k_BT}{m}$

[IIT-JAM : 2010]

Soln. $\langle \mathrm{v}_x^2 \rangle = \langle \mathrm{v}_y^2 \rangle = \langle \mathrm{v}_z^2 \rangle = \frac{k_BT}{m}$

$\langle \mathrm{v}_x \mathrm{v}_y \rangle = \langle \mathrm{v}_y \mathrm{v}_z \rangle = \langle \mathrm{v}_z \mathrm{v}_x \rangle = 0$

So, $\langle (\mathrm{v}_x - \alpha \mathrm{v}_y + \beta \mathrm{v}_z)^2 \rangle = (1+\alpha^2+\beta^2)\frac{k_BT}{m}$

Hence, correct option is (a)

Problem: Let v_x, v_y and v_z denote the components of the velocity along x-, y- and z-directions, respectively, of an ideal gas particle. At the absolute temperature T, the average value of the product $\mathrm{v}_x^2 \mathrm{v}_y^2 \mathrm{v}_z^2$ is proportional to

(a) T (b) $T^{3/2}$ (c) T^3 (d) T^6

[JNU : 2010]

Soln. $\langle \mathrm{v}_x^2\, \mathrm{v}_y^2\, \mathrm{v}_z^2 \rangle$

$$= N\left(\frac{m}{2\pi k_BT}\right)^{3/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{v}_x^2\, \mathrm{v}_y^2\, \mathrm{v}_z^2\, e^{-m(\mathrm{v}_x^2+\mathrm{v}_y^2+\mathrm{v}_z^2)/2k_BT}\, d\mathrm{v}_x\, d\mathrm{v}_y\, d\mathrm{v}_z$$

[$\because$ v_x is velocity, so limit goes from $-\infty$ to $+\infty$]

$$= N\left(\frac{m}{2\pi k_BT}\right)^{3/2} \int_{-\infty}^{\infty} \mathrm{v}_x^2\, e^{-m\mathrm{v}_x^2/2k_BT}\, d\mathrm{v}_x \int_{-\infty}^{\infty} \mathrm{v}_y^2\, e^{-m\mathrm{v}_y^2/2k_BT}\, d\mathrm{v}_y \int_{-\infty}^{\infty} \mathrm{v}_z^2\, e^{-m\mathrm{v}_z^2/2k_BT}\, d\mathrm{v}_z$$

Let $\frac{m\mathrm{v}_x^2}{2k_BT} = x \Rightarrow \mathrm{v}_x = \sqrt{\frac{2k_BT}{m}}\, x^{1/2} \Rightarrow d\mathrm{v}_x = \sqrt{\frac{2k_BT}{m}} \cdot \frac{1}{2} \cdot x^{-1/2} dx$

$$\text{So, } \int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2k_BT} dv_x = \frac{2k_BT}{m} \int_{-\infty}^{\infty} xe^{-x} \sqrt{\frac{2k_BT}{m}} \cdot \frac{1}{2} x^{-1/2} dx = \frac{2k_BT}{m} \sqrt{\frac{2k_BT}{m}} \int_0^{\infty} x^{1/2} e^{-x} dx$$

$$= \left(\frac{2k_BT}{m}\right)^{3/2} \overline{3/2} = \left(\frac{2k_BT}{m}\right)^{3/2} \cdot \frac{1}{2}\sqrt{\pi}$$

$$\text{Similarly, } \int_{-\infty}^{\infty} v_y^2 e^{-mv_y^2/2k_BT} dv_y = \int_{-\infty}^{\infty} v_z^2 e^{-mv_z^2/2k_BT} dv_z = \frac{1}{2}\left(\frac{2k_BT}{m}\right)^{3/2} \sqrt{\pi}$$

$$\left\langle v_x^2 v_y^2 v_z^2 \right\rangle = N\left(\frac{m}{2\pi k_BT}\right)^{3/2} \frac{1}{8} \cdot \left(\frac{2k_BT}{m}\right)^{9/2} \pi^{3/2} \propto T^3$$

Hence, correct option is (c)

Problem: A classical gas of molecules, each of mass m, is in thermal equilibrium at the absolute temperature T. The velocity components of the molecules along the Cartesian axes are v_x, v_y and v_z. The mean value of $(v_x + v_y)^2$ is

(a) $\frac{k_BT}{m}$ (b) $\frac{3k_BT}{2m}$ (c) $\frac{1}{2}\frac{k_BT}{m}$ (d) $\frac{2k_BT}{m}$

Soln. $\langle (v_x + v_y)^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + 2\langle v_x v_y \rangle$

Putting $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{k_BT}{m}$ $\left[\because \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{3}{2}k_BT\right]$

and $\langle v_x v_y \rangle = 0$

So, $\langle (v_x + v_y)^2 \rangle = \frac{k_BT}{m} + \frac{k_BT}{m} + 0 = \frac{2k_BT}{m}$

Hence correct option is (d).

Degree of Freedom

The total number of independent variables required to describe completely the state of motion of a body are called its *degree of freedom* (f).

It is given by $f = 3N - C$ for 3-dimension.

where N = Number of particles

C = Number of constraints (Genrally number of bonds).

(1) For monoatomic gas (e.g., Ar, Xe, Re)

$N = 1; C = 0$

So, $f = 3$ (All translational)

(2) For diatomic gas (e.g., O_2, N_2)

$N = 2; C = 1$

So, $f = 5$ (3 translational; 2 rotational)

(3) For triatomic gas

(i) linear triatomic gas (e.g., O_3)

$N = 3; C = 3$

So, $f = 6$ (3 translational; 3 rotational)

(ii) linear triatomic gas (e.g., CO_2)

$N = 3;\ C = 2$

So, $f = 7$ (3 translational; 4 rotational)

Problem: The average translational kinetic energy of O_2 (molar mass 32) molecules at a particular temperature is 0.048 eV. The translational kinetic energy of N_2 (molar mass 28) molecules in eV at the same temperature is **[IIT-JEE : 1997]**

(a) 0.0015 (b) 0.003 (c) 0.048 (d) 0.768

oln. Average translational kinetic energy of an ideal gas molecule is $3/2\, k_B T$ which depends on temperature only. Therefore, if temperature is same, translational kinetic energy of O_2 and N_2 both will be equal.

Hence, correct option is (c)

Law of Equipartition of Energy

For 1-D, the Maxwell's speed distribution function is

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_B T}}$$

So avg kinetic energy is

$$\bar{\in} = \frac{\int_{-\infty}^{\infty} \in f(v)\,dv}{\int_{-\infty}^{\infty} f(v)\,dv} = \frac{\int_{-\infty}^{\infty} \frac{1}{2} mv^2 \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_B T}} dv}{\int_{-\infty}^{\infty} \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_B T}} dv}$$

$$= \frac{m}{2} \frac{\int_{-\infty}^{\infty} v^2 e^{-\frac{mv^2}{2k_B T}} dv}{\int_{-\infty}^{\infty} e^{-\frac{mv^2}{2k_B T}} dv} = \frac{m}{2} \frac{\int_{0}^{\infty} v^2 e^{-\frac{mv^2}{2k_B T}} dv}{\int_{0}^{\infty} e^{-\frac{mv}{2k_B T}} dv}$$

Using $\int_0^\infty x^n e^{-ax^2} dx = \frac{\left|\frac{n+1}{2}\right.}{2a^{\frac{n+1}{2}}}$

$$\Rightarrow \quad \bar{\in} = \frac{m}{2} \frac{\left|\frac{3}{2}\right. 2\left(\frac{m}{2k_B T}\right)^{3/2}}{\left|\frac{1}{2}\right. 2\left(\frac{m}{2k_B T}\right)^{1/2}} = \frac{m}{2} \frac{\frac{1}{2}\sqrt{\pi}}{\sqrt{\pi}} \frac{2k_B T}{m}$$

$$\Rightarrow \quad \bar{\in} = \frac{1}{2} k_B T$$

Thus, in thermal equilibrium, any degree of freedom (such as component of the position or velocity of a particle) which appears only "quadratically" in the energy has an average energy per molecule of $\frac{1}{2} k_B T$.

This is the *law of equipartition of energy*

- Average energy per molecule

$$U = \frac{f}{2}k_BT \qquad \ldots (28)$$

- Average energy per mole

$$U = N_A\frac{f}{2}k_BT = \frac{f}{2}RT \qquad [\because\ R = k_BN_A]$$

Problem: A system of N non-interacting classical point particles constrained to move on the two-dimensional surface of a sphere. The internal energy of the system is

(a) $\frac{3}{2}Nk_BT$ (b) $\frac{1}{2}Nk_BT$ (c) Nk_BT (d) $\frac{5}{2}Nk_BT$

Soln. Since, particle is moving on two-dimensional surface its degree of freedom = 2
Hence, for N non-interacting particle total degree of freedom = $2N$
The energy per degree of freedom = $1/2\ k_BT$

Hence, total energy $U = 2N \times \frac{1}{2}k_BT$

$\Rightarrow U = Nk_BT$

Hence, the correct option is (c).

Problem: A system of N classical non-interacting particles, each of mass m, is at a temperature T and is confined by the external potential $V(r) = \frac{1}{2}Ar^2$ (where A is a constant) in three dimensions. The internal energy of the system is

(a) $3Nk_BT$ (b) $\frac{3}{2}Nk_BT$

(c) $N(2mA)^{3/2}k_BT$ (d) $N\sqrt{\frac{A}{m}}\ln\left(\frac{k_BT}{m}\right)$

Soln. The contribution of thermal energy with each quadratic term in Hamiltonian is $\frac{1}{2}k_BT$.

The Hamiltonian of a classical particle $H = \frac{p^2}{2m} + \frac{1}{2}Ar^2$

In 3-D, hamiltonian has 6 quadratic term. So, the internal energy of a particle is $6 \times \frac{1}{2}k_BT = 3k_BT$

The internal energy of a system of N particles = $3Nk_BT$.

Correct answer is (a)

Problem: A vessel contains a mixture of one mole of oxygen and two moles of nitrogen at 300 K. The ratio of the average rotational kinetic energy per O_2 molecule to per N_2 molecule is

(a) 1 : 1 (b) 1 : 2 (c) 2 : 1

(d) depends on the moment of inertia of the two molecules

[IIT-JEE : 1998]

Soln. Average kinetic energy per molecule per degree of freedom = $1/2\, k_B T$. Since, both the gases are diatomic and at same temperature (300 K), both will have the same number of rotational degree of freedom i.e., two. Therefore, both the gases will have the same average rotational kinetic energy per molecule = $2 \times 1/2\, k_B T$ or $k_B T$. Thus ratio will be 1 : 1.

Correct option is (a).

Problem: A gas mixture consists of 2 moles of oxygen and 4 moles of argon at temperature T. Neglecting all vibrational modes, the total internal energy of the system is

(a) $4\,RT$ (b) $15\,RT$ (c) $9\,RT$ (d) $11\,RT$

[IIT-JEE : 1999]

Soln. Internal energy of n moles of an ideal gas at temperature T is given by

$$U = n\left(\frac{f}{2}RT\right)$$

where, f = degree of freedom.
= 5 for O_2 and 3 for Ar

Hence, $$U = U_{O_2} + U_{Ar} = 2\left(\frac{5}{2}RT\right) + 4\left(\frac{3}{2}RT\right) = 11\,RT.$$

Correct option is (d)

Problem: At a given temperature, T, the average energy per particle of a non-interacting gas of two-dimensional classical harmonic oscillator is _____ $k_B T$.

Soln. According to two-dimensional harmonic oscillator, we consider the vibration of molecules in two dimensions. Vibrational mode in one dimension provides $k_B T$ energy. In two dimension, total energy is vibrational molecules.

Hence, 2 is correct answer = $2 \times (k_B T)$ energy.

Specific Heat Capacity

- The "molar" specific heat at constant volume is

$$C_V = \left(\frac{dU}{dT}\right)_V = \frac{f}{2}R \quad \text{... (29)}$$

CAREER ENDEAVOUR

- Also, the molar specific heat at constant pressure is

$$C_P = C_V + R = \left(\frac{f}{2} + 1\right)R \quad \text{... (30)}$$

- Also, the ratio of C_P and C_V is

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f} \quad \text{... (31)}$$

(1) For monoatomic gas, $(f = 3)$

$$U = \frac{3}{2}RT;\quad C_V = \frac{3}{2}R;\quad C_P = \frac{5}{2}R;\quad \gamma = \frac{5}{3} = 1.67$$

(2) For diatomic gas $(f = 5)$

$$U = \frac{5}{2}RT;\quad C_V = \frac{5}{2}R;\quad C_P = \frac{7}{2}R;\quad \gamma = 1 + \frac{2}{5} = \frac{7}{5} = 1.40$$

(3) For triatomic non-linear gas $(f = 6)$

$$U = \frac{6}{2}RT;\quad C_V = \frac{6}{2}R;\quad C_P = \frac{8}{2}R;\quad \gamma = 1 + \frac{2}{6} = \frac{4}{3} = 1.33$$

(4) For triatomic linear gas $(f = 7)$

$$U = \frac{7}{2}RT;\quad C_V = \frac{7}{2}R;\quad C_P = \frac{9}{2}R;\quad \gamma = 1 + \frac{2}{7} = \frac{9}{7} = 1.28$$

Problem: Consider oxygen gas at room temperature and pressure and assume that only translational and rotational motions of the molecules contribute to the specific heat. If C_P and C_V denote respectively, specific heats at constant pressure and volume, then the ratio C_P/C_V is

(a) $\frac{3}{5}$ (b) $\frac{5}{3}$ (c) $\frac{5}{7}$ (d) $\frac{7}{5}$ **[IISc : 2006]**

Soln. $\gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}$

when f is degree of freedom

There are two degree of freedom associated with rotational motion and three degree of freedom associated with translational motion.

So, total number of degree of freedom associated with motion of diatomic molecule, $f = 5$

So, $\gamma = 1 + \frac{2}{5} = 1.4$

Hence, correct option is (d)

Problem: Keeping density and sound speed constant, doubling the pressure implies that the ratio of specific heats C_P/C_V. **[IISc : 2009]**

(a) doubles (b) halves (c) remains constant (d) quadruples

Soln. Velocity, $v = \sqrt{\frac{\gamma P}{\rho}} \Rightarrow \gamma = \frac{\rho v^2}{P}$

Keeping ρ and v same and doubling pressure will halves γ.

Hence, correct option is (b)

Mean Free Path

In the assumption of kinetic theory of gases, we assumed that the molecules of gas are moving with very high velocity, which means, that molecules of gas contained in vessel should disappear in no time which is contrary to actual observation, because of absence of force to restrain their motion. Thus there was a serious objection against the assumption that the molecules of a gas move with large rectilinear velocities. This difficulty was solved by the Clausius who assumed that the molecules of a gas have a small, but finite size. These molecule collide with one another after short intervals resulting in a change in both the magnitude and direction of the velocities of the molecules.

Since there is no force acting on the molecules except during collision, they move in straight lines with constant speeds between two successive collision. Thus the paths of diffierent molecules is a series of short zig-zag paths of different length. These paths of different length are called the *free paths* of the molecule and their mean is called *mean free path*.

- The *mean free path* is defined as the average distance travelled by a molecule between two successive collision.
- It is given by

$$\boxed{\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n}} \quad \ldots (32)$$

where d is the diameter of the molecule and n is the particle density i.e. number of molecules per unit volume.

- $\lambda = \dfrac{N}{\sqrt{2}\,\pi d^2 V} \qquad \left[\because \quad n = \dfrac{N}{V}\right]$ ... (33)
- $\lambda = \dfrac{k_B T}{\sqrt{2}\,\pi d^2 P}$ ... (34)

where we have used $PV = Nk_BT$

- The *collision time* is defined as the time between two successive collision. It is equals to

$$\tau = \frac{\lambda}{\bar{v}} = \frac{k_B T}{\sqrt{2}\,\pi d^2 P\bar{v}} = \frac{1}{\sqrt{2}\,\pi d^2 n\bar{v}} \quad \text{... (35)}$$

where $\bar{v}$ is the average speed of the molecules

- The *collision frequency* is defined as the number of collisions in one second. It is equals to

$$= \frac{1}{\tau} = \sqrt{2}\,\pi d^2 n\bar{v}$$

- Note: The $\bar{v}$ is usually taken to be v_{rms}.

Problem: At what pressure will the mean free path be 50 cm for spherical molecules of radius 3×10^{-10}m? Assume an ideal gas at 20°C.

Soln. From the expression for the mean free path we obtain.

$\dfrac{N}{V} = \dfrac{1}{4\pi\sqrt{2}\,b^2\lambda}$ where λ = mean free path.

Combining this with the ideal gas law in the form $PV = Nk_BT$ gives

$$P = \frac{k_B T}{4\pi\sqrt{2}\,b^2\lambda} = \frac{(1.38\times10^{-23}\,J/K)(293K)}{4\pi\sqrt{2}(3.0\times10^{-10}m)^2(0.50m)} = 5.1mPa$$

Problem: At what pressure will the mean free path be 50 cm for spherical molecules of radius 3×10^{-10}m? Assume an ideal gas at 20°C.

Soln. From the expression for the mean free path we obtain.

$\dfrac{N}{V} = \dfrac{1}{4\pi\sqrt{2}\,r^2\lambda}$, where, λ = mean free path.

CAREER ENDEAVOUR

Combining this with the ideal gas law in the form $PV = Nk_BT$ gives

$$P = \frac{k_B T}{4\pi\sqrt{2}\,b^2\lambda} = \frac{(1.38\times10^{-23}\,J/K)(293K)}{4\pi\sqrt{2}(3.0\times10^{-10}m)^2(0.50m)} = 5.1mPa$$

Problem: Estimate the mean free path of a molecule of air t 27 °C and 1 atm. Model the molecules as sphere with radius $r = 2.0 \times 10^{-10}$ m.

(a) 5.8×10^{-9}m (b) 5.8×10^{-8}m (c) 5.8×10^{-10}m (d) 5.8×10^{-7}m

Soln. Given: $T = 27\,^\circ\text{C} = 300$ K, $P = 1$ atm $= 1.013\times10^5$ N/m^2, $r = 2.0\times10^{-10}$ m

The mean free path is $\lambda = \dfrac{k_B T}{\sqrt{2}\pi d^2 P}$, where d is the diameter of the molecules $= 2r$

$$\therefore\ \lambda = \frac{k_B T}{4\sqrt{2}\pi r^2 P} = 5.8\times10^{-8}\ \text{m}$$

Correct option is (b)

PROBLEMS TO BE PLAYED

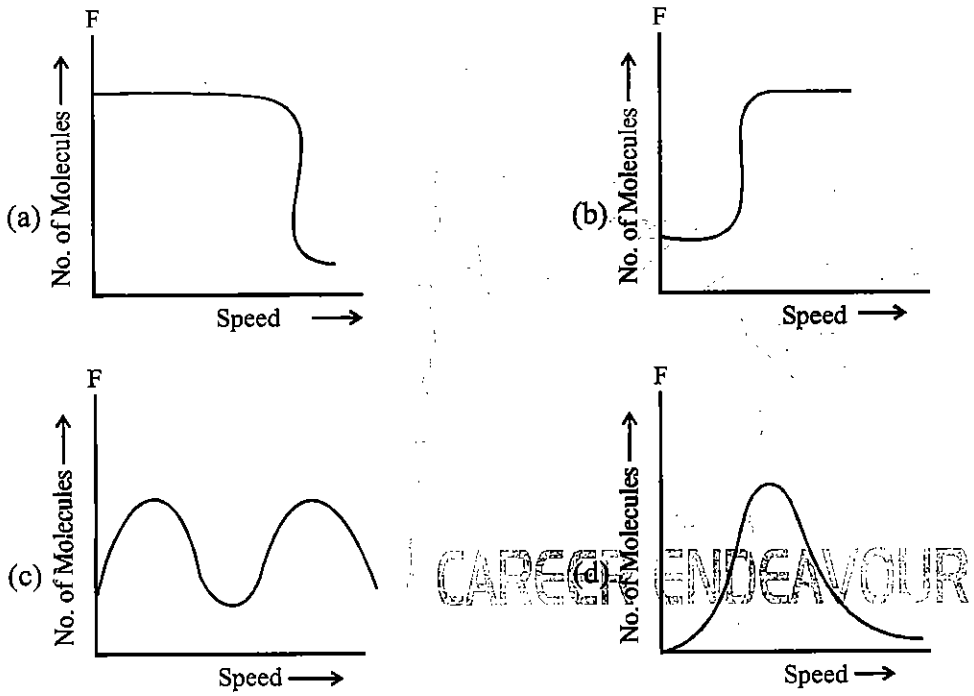
1. For polyatomic gases such as hydrogen the corresponding degree of freedom would be–
(a) Two, three (b) Five, six (c) Three, nine (d) Three, four

2. The ratio of two specific heats of a diatomic gas is–
(a) 1.66 (b) 1.33 (c) 1.40 (d) 1.52

3. If the degree of freedom of a gas is n, then the ratio of C_p and C_v is–
(a) $1+\frac{2}{n}$ (b) $1+\frac{1}{n}$ (c) $1+\frac{1}{2n}$ (d) $\frac{2n}{2n+1}$

4. In a gas the expression for the average speed of molecule is given by–
(a) $\sqrt{\frac{3k_BT}{m}}$ (b) $\sqrt{\frac{2k_BT}{m}}$ (c) $\sqrt{\frac{8k_BT}{m}}$ (d) $\sqrt{\frac{3k_BT}{2m}}$

5. Which of the following curves represents Maxwell's distribution law of speed of molecules?



CAREER ENDEAVOUR

6. The gas exerts pressure on the walls of the container because the gas molecules–
(a) Have finite size (b) Obey Boyle's law
(c) Have momentum (d) Collide with one another

7. The most probable speed v_{mp} and the root mean square speed 'c' are related by–
(a) $v_{mp}=\sqrt{\frac{1}{2}}c$ (b) $v_{mp}=\sqrt{\frac{2}{3}}c$ (c) $v_{mp}=\sqrt{\frac{3}{8}}c$ (d) $v_{mp}=\sqrt{\frac{1}{3}}c$

8. The speed of sound V_s in a gas, *r.m.s.* speed of the molecule of a gas V_{rms} and the ratio of specific heats γ of the gas is related by
(a) $V_s = V_{(rms)}$ (b) $V_s = V_{rms}\times\sqrt{3/\gamma}$ (c) $V_s = V_{rms}\sqrt{\gamma}$ (d) $V_s = V_{rms}\sqrt{\gamma/3}$

9. The mean free path is
(a) Inversely proportional to the pressure (P) (b) directly proportional to the pressure
(c) proportional to P^2 (d) proportional to P^4

10. The correct expression for the most probable velocity of the molecules of a gas in a steady state is given by
(a) $\left(\frac{2}{3}\right)^{1/2}$ r.m.s. speed (b) equal to r.m.s. speed
(c) $\frac{2}{3}$ r.m.s speed (d) $\left(\frac{3}{2}\right)^{1/2}$ r.m.s. speed

11. According to the kinetic theory of gases, pressure exerted by a perfect gas is equal to
(a) $\frac{1}{2}mv^2$, where v is average velocity (b) mgh
(c) $\frac{2}{3}$E, where E is the mean kinetic energy per unit volume of gas
(d) all of these

12. Assuming the Maxwellian distribution of speeds for molecules of a liquid also, at temperature below the normal boiling point of a liquid
1. molecules with higher speeds escape from the surface of the liquid.
2. molecules with lower speeds escape from the surface
3. average kinetic enegy of the molecules is the liquid increases as evaporation proceeds
4. average kinetic energy decreases with evaporation
(a) 2 and 3 (b) 1 and 4 (c) 2 and 4 (d) 1 and 3

13. Maxwell's law of distribution of speed show that the number of molecules with average speed is
(a) Very small (b) large (c) zero (d) exactly equal to 1.

14. The root-mean square speed of a particle of mass m in the kinetic theory is given by
(a) $\sqrt{\frac{k_B T}{m}}$ (b) $\sqrt{\frac{2k_B T}{m}}$ (c) $\sqrt{\frac{3k_B T}{m}}$ (d) $\sqrt{\frac{8k_B T}{m}}$

15. Specific heats of a gas at constant volume (C_V) and at constant pressure (C_p) are related as–
(a) $\frac{C_P}{C_V} = 1 - \frac{R}{J}$ (b) $C_P - C_V = \frac{R}{J}$ (c) $C_P - C_V = \frac{J}{R}$ (d) $C_P - C_V = \frac{R}{J}$

16. If molar $C_p = 4.97$ cal/mole, then
(a) $C_v = 2.97$ (b) $C_v = 1.97$ (c) $C_v = 5.97$ (d) $C_v = 0.97$

ANSWER KEY

1. (a)	**2. (c)**	**3. (a)**	**4. (c)**	**5. (d)**	**6. (c)**	**7. (b)**
8. (d)	**9. (a)**	**10. (a)**	**11. (c)**	**12. (b)**	**13. (b)**	**14. (c)**
15. (b)	**16. (a)**					

Chapter 2

The Gas Laws & the First Law of Thermodynamics

The Gas Laws

(1) Boyle's Law:

- "At constant temperature, the pressure of a fixed amount (i.e. number of moles n) of gas varies inversely with its volume.

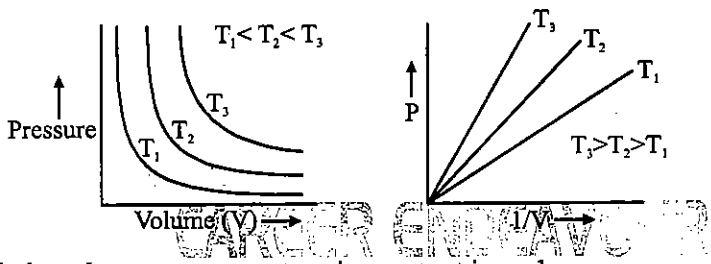
Mathematically, $P \propto \frac{1}{V}$ (at constant T and n) ... (1)

$\Rightarrow$ $\boxed{PV = \text{Constant}}$ ... (2)

$\Rightarrow$ $P_1V_1 = P_2V_2$ ... (3)

where constant depends upon the amount of gas, temperatue of the gas and the units in which P and V are expressed.

- The variation of pressure with volume and its inverse is



Each graph is called *isotherm* as temperature is constant in each one.

- Equation (2) $\Rightarrow$ $\frac{Pm}{\rho} = \text{Constant}$; $\rho \rightarrow$ density of gas

$\Rightarrow$ $P = \rho \times \text{Constant}$

At constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

Problem: A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 per pressure the gas occupies 2.27 L volume, upto what volume can the baloon be expanded?

Soln. Given: $P_1 = 1$ bar, $V_1 = 2.27$ L and $P_2 = 2$ bar, $V_2 = ?$

Using Boyle's law, $P_1V_1 = P_2V_2 \Rightarrow V_2 = \frac{P_1}{P_2}V_1 = \frac{1}{0.2} \times 2.27\text{ L} = 11.35\text{ L}$

Correct option is (a)

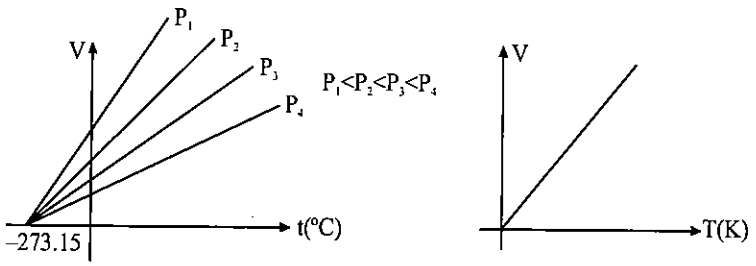
(2) Charle's Law:

- "For a fixed mass of a gas at constant pressure, volume of a gas is directly related to the absolute temperature."

Mathematically, $V \propto T$ ... (4)

Or $\boxed{\frac{V}{T} = \text{Constant}}$ ... (5)

- The variation of volume with temperature in Kelvin and Celsius is



(1) Each Graph is called *isobar* as pressure is constant in all graphs.
(2) All the lines meet the temperature aries at –273.15°C.

Problem: On a ship sailing in Pacific Ocean where temperature is 23.4 °C, a balloon is filled with 2 L air. What will be the volume of the balloon when the ship reaches Indian Ocean where temperature is 26.1 °C ?

(a) 201.8 L (b) 20.18 L (c) 0.2018 L (d) 2.018 L

Soln. Given : $T_1 = 23.4\,°C = (23.4 + 273)\,K = 296.4\,K$

$V_1 = 2\,L$

$T_2 = 26.1\,°C = (26.1 + 273)\,K = 299.1\,K$

$V_2 = ?$

Since the pressure during the sailing remains constant due to the atmosphere. i.e., atmospheric pressure, the pressure remains constant. So using Charle's law, we have

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

CAREER ENDEAVOUR

$$\Rightarrow V_2 = \frac{T_2}{T_1} V_1 = \frac{299.1}{296.4} \times 2 = 2.018\,L$$

Correct option is (d)

(3) Avagadro Law

- "Equal volume of all gases under the same conditions of temperature and pressure contain the equal number of molecules".

Mathematically, $V \propto N \Rightarrow V \propto n \quad [\because N = nN_A]$ ... (6)

Or, $\boxed{\frac{V}{n} = \text{constant}}$ ... (7)

where number of moles $= \frac{w}{W}$

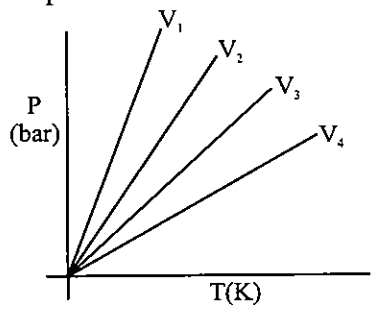
where, w = Given mass
W = Molar mass

(4) Gas-Lussac's Law:

- "At constant volume, pressure of a fixed amount of gas varies directly with the temperature."
  Mathematically, $P \propto T$ ... (8)

Or $\boxed{\frac{P}{T} = \text{Constant}}$ ... (9)

- The variation of pressure with temperature is



- Each graph is called *isochore* as volume is constant in all graphs.

The Ideal-Gas Equation:

The three gas-laws are

$N \propto P$ (Boyle's law)

$V \propto T$ (Charle's law)

$V \propto n$ (Avagadro's law)

Combining, we have

$$V \propto \frac{nT}{P}$$

$$\Rightarrow V = \frac{RnT}{P}; \quad \text{where R = Universal Gas constant}$$

$$\Rightarrow \boxed{PV = nRT} \quad \text{... (10)}$$

This is called an *ideal gas equation*.

CAREER ENDEAVOUR

Problem: A balloon will carry a total load of 175 kg when the temperature and pressure are normal. What load will the balloon carry on rising to a height at which the barometric pressure is 50 cm of mercury and the temperature is –10 °C, assuming the envelope maintains a constant volume ?

(a) 1195.0 kg (b) 119.5 kg (c) 11.95 kg (d) 1.195 kg

Soln. Using $\frac{\rho V}{T} = \text{constant}$, we have

$$\Rightarrow \frac{\rho_1 V_1}{T_1} = \frac{\rho_2 V_2}{T_2}$$

Here, $\rho_1 = \frac{M_1}{V}$ and $\rho_2 = \frac{M_2}{V}$

$$\therefore \quad \frac{M_1}{M_2} = \frac{\rho_1}{\rho_2} = \frac{P_1 T_2}{P_2 T_1} \Rightarrow M_2 = \frac{P_2}{P_1}\frac{T_1}{T_2} M_1 = \frac{50}{76} \times \frac{273}{263} \times 175 = 119.5\ kg$$

Problem: A monoatomic gas is described by the equation of state $P(V - bn) = nRT$, where b and R are constants and other quantities have their usual meanings. The maximum density (in moles per unit volume to which this gas can be compressed is

(a) $\frac{1}{bn}$ (b) b (c) $\frac{1}{b}$ (d) infinity

Soln. Given : $P(V - bn) = nRT$

$$\Rightarrow PV - Pbn = nRT \Rightarrow n = \frac{PV}{Pb + nRT}$$

So density, $\rho = \frac{n}{V} = \frac{P}{Pb + nT}$

For maximum of ρ,

$$\frac{d\rho}{dP} = \frac{(Pb + nT)1 - P(b)}{(Pb + nT)^2} = 0 \Rightarrow nT = 0$$

$$\therefore \rho = \frac{P}{Pb} = \frac{1}{b}$$

Correct option is (c)

Problem: An ideal gas expands in a process in which its pressure depends on the volume as $p = p_0 e^{-\alpha V}$, where p_0 and α are two positive constants. In n is the number of moles in the gas, the maximum temperature that it will attain in this process is (R is the universal gas constant)

(a) $p_0/e\,\alpha nR$ (b) $p_0/\alpha n^3 R$ (c) $ep_0/\alpha nR$ (d) $p_0^2/\alpha nR$

[JNU : 2009]

Soln. $p = p_0 e^{-\alpha V}$

So, $T = \frac{pV}{nR} = \frac{p_0 e^{-\alpha V} \cdot V}{nR}$

To maximise T, take its derivative and make it equals to zero

$$\frac{dT}{dV} = \frac{p_0}{nR}\left[e^{-\alpha V} - \alpha V e^{-\alpha V}\right] = 0$$

$$\Rightarrow \quad V = \frac{1}{\alpha}$$

Now, $\frac{d^2T}{dV^2} = \frac{p_0}{nR}\left[-\alpha e^{-\alpha V} - \alpha e^{-\alpha V} + \alpha^2 V e^{-\alpha V}\right] < 0$ for $V = \frac{1}{\alpha}$

So, $T_{max} = \left.\frac{p_0 e^{-\alpha V} \cdot V}{nR}\right|_{V=\frac{1}{\alpha}} = \frac{p_0}{e\alpha nR}$

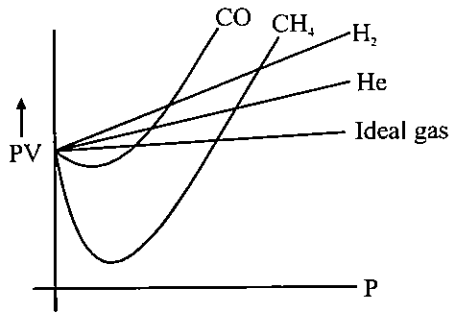
Hence, correct option is (a)

Deviation from ideal gas behavior:

A gas which obeys the gas laws and the gas equation $PV = nRT$ strictly at all temperature and pressure is said to be an *ideal gas*. The molecules of ideal gases are assumed to be volume less points with no attractive forces between one another. But no real gas strictly obeys the gas equation at all temperatures and pressures. Deviation from ideal behavior are observed particularly at high pressures or low temperatures.

The deviation from ideal behavior is expressed by introducing a factor Z known as *compressibility factor* in the ideal gas equation. Z may be expressed as $Z = \frac{PV}{nRT}$

- In case of ideal gas, $PV = nRT$. $\therefore Z = 1$
- In case of real gas, $PV \neq nRT$. $\therefore Z \neq 1$



- When $Z < 1$, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behavior.
- When $Z > 1$, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behavior.

Causes of Deviation from Ideal Behavior

1. The volume occupied by gas molecules is not negligible as compared to the volume occupied by the gas.
2. The forces of attraction between gas molecules are negligible.

Problem: One mole of SO_2 occupies a volume of 350 mL at 300 K and 50 atm pressure. Calculate the compressibility factor of the gas.

Soln. $Z = \frac{PV}{nRT} = \frac{50 \times 1.01 \times 10^5 \times 0.350 \times 10^{-3}}{1 \times 8.314 \times 300} = 0.71.$

Thus, SO_2 is more compressibility than expected from ideal behavior.

Different forms of van der Waals' equation

1. **At very low pressure :** V becomes so large that both b and a/V^2 become negligible and the van der Waals' equation reduces to

   $$\left(P + \frac{a}{V^2}\right)(V - b) = RT \Rightarrow PV = RT$$

   Gases approach ideal behavior at very low pressure.

2. **At low pressure :** V is large and 'b' is negligible in comparison with V.

   Therefore, $\left(P + \frac{a}{V^2}\right)V = RT \Rightarrow PV + \frac{a}{V} = RT$

   $$\Rightarrow \quad PV = RT - \frac{a}{V} \text{ or } \frac{PV}{RT} < 1 - \frac{a}{RTV} \text{ or } \frac{PV}{RT} < 1$$

   This accounts for the dip in isotherm at low pressure.

3. **At fairly high pressure :** $\frac{a}{V^2}$ may be neglected in comparison with P.

Therefore, $P(V-b)=RT \Rightarrow \frac{PV}{RT}=1+\frac{Pb}{RT}>1$

This accounts for the rising parts of the isotherm at high pressure.

Hydrogen and Helium are two lightest gases known. Their molecules have very small masses. The attractive forces between such molecules will be extensively small. So a/V^2 is negligible even at ordinary pressure.

Thus, $\frac{PV}{RT}>1$, even at low pressure.

Prob. One litre of a gas at 300 atm and 473 K is compressed to a pressure of 600 atm and 273 K. The compressibility factors found are 1.072 and 1.375 respectively at initial and final states. Calculate the final volume.

Soln. $P_1V_1 = Z_1\, nRT_1$ and $P_2V_2 = Z_2\, nRT_2$

$$\therefore \frac{P_1V_1}{Z_1T_1}=\frac{P_2V_2}{Z_2T_2} \Rightarrow V_2=\frac{P_1V_1Z_2T_2}{P_2Z_1T_1}$$

$$\Rightarrow V_2=\frac{300}{600}\times\frac{1.375}{1.072}\times\frac{273}{473}\times 1\,\text{L}=370.9\,\text{mL}.$$

vander Waal Gas (The Real Gas)

(1) Correction in pressure :

Due to the presence of molecular attraction the molecule striking the wall of container is pulled back by the other molecules, and hence the observed pressure on the face of wall is less than the actual pressure within the body of the gas. The decrease in pressure p is proportional to

- Number of attracting molecules / Volume.
- Number of molecules striking per unit area of the wall of the container per second.

Decrease in pressure, $p \propto \frac{1}{\rho^2} \propto \frac{1}{V^2} \Rightarrow p=\frac{a}{V^2}$

Real pressure $= p + p = P + \frac{a}{V^2}$

(2) Correction in Volume:

Since the particles have finite size the volume left for the particles for their free movement is less than actual volume V. If b is the volume occupied by the size of the particle, then

free volume $= V - b$

So, from ideal gas equation PV = RT, we have

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \qquad \ldots (11)$$

For n mole, $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$ ... (12)

Equations (11) and (12) are called *vander Waal gas equation* for one mole and n moles respectively.

Problem: A real gas behaves like an ideal gas if its
(a) pressure and temperature are both high
(b) pressure and temperature are both low
(c) pressure is high and temperature is low
(d) pressure is low and temperature is high **[IIT-JEE : 2010]**

Soln. A real gas behaves like an ideal gas at low pressure and high temperature.
Hence, correct option is (d).

Different Types of Temperature in Thermodynamics

(1) Boyle's Temperature (T_b)

It is a temperature at which vander Waal gas behave like an ideal gas.

If at $T = T_b$, the Vander Waal's equation i.e. $PV = RT$, then

$$\frac{RT_bV}{V-b} - \frac{a}{V} = RT_b \Rightarrow RT_b\left(\frac{V}{V-b} - 1\right) = \frac{a}{V}$$

$$\Rightarrow RT_b = \frac{a}{b}\left(\frac{V-b}{V}\right) \Rightarrow T_b = \frac{a}{Rb}\left(\frac{1-b}{V}\right) = \frac{a}{Rb}\left(1 - \frac{b}{V}\right)$$

Since b << V, so $\boxed{T_b = \frac{a}{Rb}}$

(2) Critical temperature (*Tc*)

It is the temperature above which a gas can't be liquified by the application of pressure alone.
According to vander Waal gas equation

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \Rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Now $\left(\frac{dP}{dV}\right)_{T=T_C} = -\frac{RT_C}{(V_C-b)^2} + \frac{2a}{V_C^3} = 0 \Rightarrow \frac{2a}{V_C^3} = \frac{RT_C}{(V_C-b)^2}$ ... (14)

Again differentiating

$$\left(\frac{d^2P}{dV^2}\right)_{T=T_C} = \frac{2RT_C}{(V_C-b)^3} - \frac{6a}{V_C^4} = 0$$

$$\Rightarrow \frac{2RT_C}{(V_C-b)^3} = \frac{6a}{V_C^4}$$

Using (14), $\frac{V_C}{3} = \frac{V_C-b}{2} \Rightarrow V_C = 3b$ ... (15)

Using (15) in (14), $T_C = \frac{2a \cdot 4b^2}{27b^3R} \Rightarrow T_C = \frac{8a}{27Rb}$ ... (16)

Using (16) in vander Waal's equation

$$P_C = \frac{a}{27b^2}$$

where the *critical pressure* of a substance is the pressure required to liquefy a gas at its critical temperature

Also, $\frac{P_CV_C}{T_C} = \frac{a}{27b^2} \cdot \frac{3b}{8a} \cdot 27Rb = \frac{3R}{8}$ ... (17)

Problem: The equation of state for a gas is given by $\left[p+\left(\frac{\alpha N}{V}\right)^2\right](V-\beta N)=N k_B T$, where p, V, T, N and k_B respectively represent pressure, volume, temperature, number of atoms and the Boltzmann constant, respectively, while α and β are constants specific to the gas.

If the critical point C corresponds to a point of inflexion of the p-V curve, then the critical volume V_c and the critical pressure p_c, for this gas are given by

(a) $V_c=3\beta N,\ p_c=\frac{\alpha^2}{3\beta^2}$ (b) $V_c=3\beta N,\ p_c=\frac{\alpha}{27\beta^2}$

(c) $V_c=3\beta N,\ p_c=\frac{8\alpha^2}{27\beta}$ (d) $V_c=3\beta N,\ p_c=\frac{\alpha^2}{27\beta^2}$

Soln. Given: $\left[p+\left(\frac{\alpha N}{V}\right)^2\right](V-\beta N)=N k_B T$

Comparing with vander Waals' equation

$$\left(p+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

or in terms of number of molecules (N),

$\left(p+\frac{aN^2}{\gamma^2}\right)(V-Nb)=N k_B T$, we have $a=\alpha^2,\ b=\beta$

So $V_c=3Nb=3N\beta$

$$p_c=\frac{a}{27b^2}=\frac{\alpha^2}{27\beta^2}$$

Correct option is (c)

Terms in Thermodynamics

1. **Thermodynamics :** It is the branch of physics that deals with the concepts of heat and temperature and the inter conversion of heat and other forms of energy.
   - It is a macroscopic science. It deals with bulk systems and does not go into the molecular constitution of matter.
2. **System:** According to Oxford dictionary, a *system* is defined as complex whole set of connected things or parts.
3. **Thermodynamic systems:** A definite quantities of substance bounded by some closed surface is known as a *system*.
   A system always interacts with the environment surrounding the system. Thus, surrounding has to play a considerable/significant role in affecting the working of the system.
4. **State of a system:** The quantities which are used to determine the characteristic of a system are said to be the *state* of a system.

The equation connecting the pressure, volume and the absolute temperature of a gas is called the equation of state of that gas. Mathematically, the equation of state is represented as

$$F(P,V,T)=0$$

5. **Equilibrium :** If the macroscopic variables (P, V, T) that characterise the system do not change in time, the system is said to be in an *equilibirium*.
   (i) If T is not changing with time → Thermal Equilibrium
   (ii) If P is not changing with time → Mechanical Equilibrium
   (iii) If composition is not changing with time → Chemical Equilibrium

6. **Quasi-static process:** A *quasi-static* process is defined as the process in which the deviation from thermodyanmic equilibrium is infinitesimal and all the state through which the system passes may beconsidered as the succession of equilbrium states e.g. if a turbine is moved at infinitesimally slow rate, the system is at all time in quiescent equilibrium state and then process can be considered *quasi-static*.

7. **Reversible process :** A *reversible process* is one which can be reversed in such a way that all changes taking place in the direct process are exactly repeated in the opposite order and sense and no changes are left in any of the bodies taking part in the process or in the surrounding.

The condition for reversibility :

A process can be reversible only when it satisfy two conditions

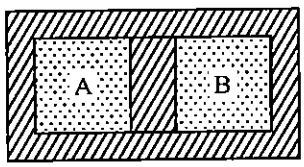
(i) Process must be quasistatic (If the process is performed in such a way that at any instant during the process the system is very nearly in the thermodynamic equilibrium).
A quasistatic process is an idealised process in which all changes take place infinitely and slowly.

(ii) Process must be non-dissipiative (dissipiative force such as friction, resistance, hysteresis etc must be completely absent).

8. **Irreversible Process:** Any process inevitably is an irreversible process because we always have some departure from initial system in carrying out the process again. Thus, those processes which produce a permanent change in the thermodynamic state of the system and cannot be retraced in the opposite order are known as *irreversible process*.

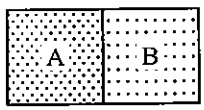
Types of Walls

(1) Adiabatic Wall : It is an insulating wall (can be movable) that does not allow flow of energy (heat) from one system to another.



All possible pairs (P_A, V_A) and (P_B, V_B) are in equilibrium.

(2) Diathermal Wall : It is a conducting wall that allows energy (heat) from system to another.



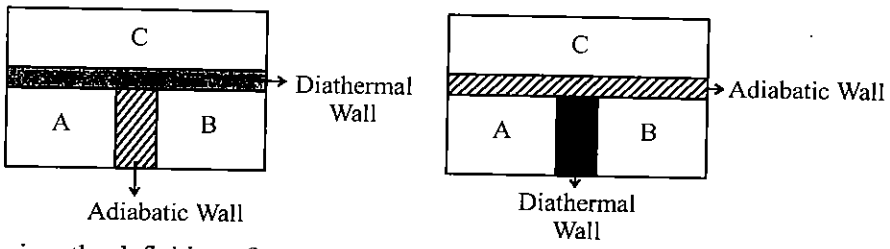
After the exchange of heat, a new equilibrium state is achieved i.e.

$(P_A, V_A), (P_B, V_B) \Rightarrow (P'_A, V'_A)$ and (P'_B, V'_B)

Zeroth Law of Thermodynamics

"It states that two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other."

Suppose there are three systems A, B and C. If initially, there is an adiabatic wall between A and B, and a diathermal wall between both A and C, and B and C as shown in the figure. Then after some time, the systems A and B both will be in thermal equilibrium with system C individually. Now, we have interchanged the adiabatic and diathermal wall as shown in the figure below. Then, we observed that A and B are already in thermal equilibrium.



- This law gives the definition of temperature.
- Mathematically, if $T_A = T_C$ and $T_B = T_C$

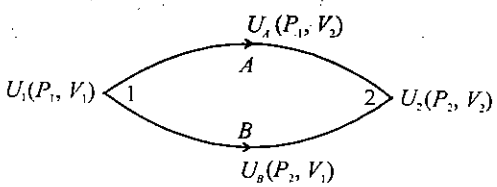
$\Rightarrow T_A = T_B$

i.e. system A and system B are also in thermal equilibrium

- Temperature is the marker of the hotness and coldness of a body.
- Heat flows from a body at high temperature to a body at low temperature. The flow stops when the temperature equalise i.e. bodies come in thermal equilibrium.

Internal Energy (U)

- It is the sum of molecular KE and PE in the frame of reference relative to which the centre of mass of the system is at rest.
- It is a state variable i.e., its value depends only on the state of the system and not on the path taken to arrive that state. For example, if you change the volume first and then pressure through the path A or change the pressure first and then volume through the path B, the change in internal energy between initial and final states remains same.



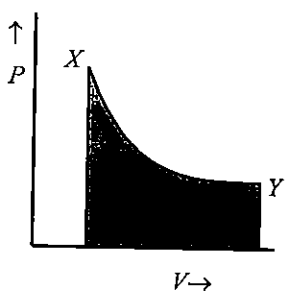
i.e. $\Delta U_{1 \xrightarrow[A]{} 2} = \Delta U_{1 \xrightarrow[B]{} 2}$

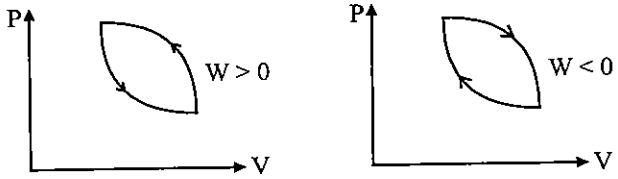
Work (W)

- It is defined as

$$\boxed{W = \int_{V_1}^{V_2} P\,dV}$$

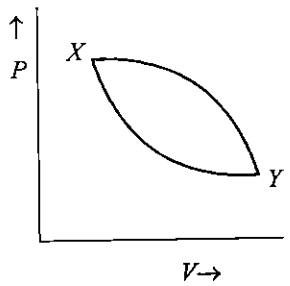
- It is a path variable i.e., depends on the path taken and given by the area in the PV-curve.





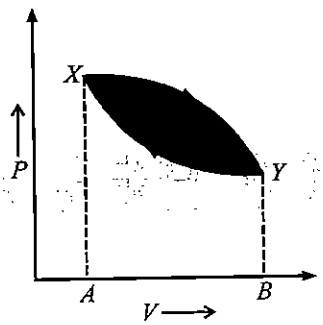
(i) Work done in anti-clockwise direction is positive and done by the system.
(ii) Work done in clockwise direction is negative and done on the system.

Problem: A piston containing an ideal gas is originally in the state X (see figure). The gas is taken through a thermal cycle $X \rightarrow Y \rightarrow X$ as shown:



The work done by the gas is positive if the direction of the thermal cycle is:
(a) clockwise
(b) counter - clockwise
(c) neither clockwise nor counter-clockwise
(d) clockwise from $X \rightarrow Y$ and counter-clockwise from $Y \rightarrow X$.

Soln. Since work done = Area between P-V curve and volume axis



For clockwise cycle, work done is
W = area of shaded portion (in clockwise sense)
= area of $XYBAX$ – area of $YXABY$ = positive
Hence correct option is (a).

Heat (Q)

- It is the defined as the flow of energy by virtue of the temperature difference.
- It is also a path function.
- If $\Delta Q > 0$, heat is given to the system
  If $\Delta Q < 0$, heat is taken from the system.

Sign Convention

$$\text{Work}(W) = \begin{cases} +\text{ve, by the system} \\ -\text{ve, on the system} \end{cases}$$

$$\text{Heat}(Q) = \begin{cases} +\text{ve, given to the system} \\ -\text{ve, taken away from the system} \end{cases}$$

First Law of Thermodynamics

- It is simply the principle of conservation of energy applied to the system.
- If ΔQ = Heat supplied to the system by the surroundings

  ΔW = Work done by the system on the surroundings

  ΔU = Change in internal energy of the system.

then $\Delta Q = \Delta U + \Delta W$ ... (18)

or $dQ = dU + dW$ ... (19)

where $\Delta W = P\Delta V$ ... (20)

$\Rightarrow$ $\Delta Q = \Delta U + P\Delta V$ ... (21)

Problem: A thermos bottle containing coffee is vigorously shaken and thereby the temperature of coffee rises. considering the coffee as the system, which of the following is CORRECT:

(a) $\Delta Q = 0; \Delta W < 0; \Delta U > 0$ (b) $\Delta Q = 0; \Delta W > 0; \Delta U > 0$

(c) $\Delta Q = 0; \Delta W < 0; \Delta U < 0$ (d) $\Delta Q = 0; \Delta W > 0; \Delta U < 0$

oln. Since no heat is given, $\Delta Q = 0$.

Also, the bottel is shaken and hence work is done on the bottle.

$\Rightarrow$ $\Delta W < 0$

So from first law of thermodynamic,

$\Delta U = \Delta Q - \Delta W$

$\Rightarrow$ $\Delta U = -\Delta W$ $[\because \Delta Q = 0]$

$\Rightarrow$ $\Delta U > 0$ $[\because \Delta W < 0]$

Correct option is (a)

Problem: Let ΔW be the work done in a quasistatic reversible thermodynamics process. Which of the following statements about ΔW is correct?

(a) ΔW is a perfect differential if the process is isothermal

(b) ΔW is a perfect differential if the process is adiabatic

(c) ΔW is always a perfect differential

(d) ΔW cannot be a perfect differential.

oln. According to the first law of thermodynamics $dQ = dU + dW$

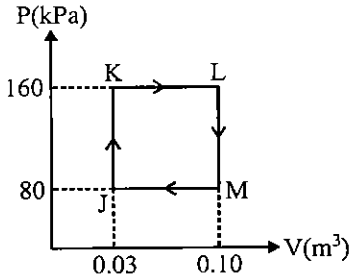
where dQ is the amount of heat absorbed by a system, dU is the change in the internal energy of the system which depends only on the temperature, and dW is the amount of work done. If $dQ \neq 0$, then dW is not a perfect differential as it depends upon the path chosen. However for an adiabatic process $dQ = 0$,

$\therefore$ $dU = -dW$

Since dU is a perfect differential, therefore dW is also a perfect differential.

Correct option is (b)

Problem: The PV diagram below represents an ideal monoatomic gas cycle for 1 mole of a gas. In terms of the gas constant R, calculate the temperatures at the points J, K, L and M.
Also calculate the heat rejected and heat absorbed during the cycle and efficiency of the cycle.



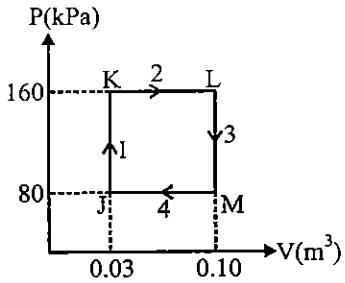
Soln. Using, $PV = nRT$ or $T = \frac{PV}{nR}$

At point K: $T = \frac{160\times10^3\times0.03}{R}$

At point L: $T = \frac{160\times10^3\times0.1}{R} = \frac{16000}{R}$

At point M : $T = \frac{80\times10^3\times0.1}{R} = \frac{8000}{R}$

At point J : $T = \frac{80\times10^3\times0.03}{R} = \frac{2400}{R}$



Total work done during the cycle = Area of loop JKLM
$= (160 - 80) \times 10^3 \times (0.1 - 0.03) = 5600J$

In process J $\rightarrow$ K,

$$dQ_1 = dU_1 + dW_1 = \frac{3}{2}R(T_K - T_J) + 0$$

$$= \frac{3}{2}R\frac{2400}{R} = 3600\ \text{J}$$

In process K $\rightarrow$ L,

$$dQ_2 = dU_2 + dW_2$$

$$= \frac{3}{2}R(T_L - T_K) + 160\times10^3(0.1-0.03) = \frac{3}{2}R.\frac{11200}{R} + 11200 = 28000J$$

In process L $\rightarrow$ M,

$$dQ_3 = dU_3 + dW_3 = \frac{3}{2}R(T_M - T_L) + 0$$

$$= \frac{3}{2}.R.\left(\frac{-8000}{R}\right) = -12000J$$

In process, M $\rightarrow$ J,

$$dQ_4 = \frac{3}{2}R(T_J - T_M) + 80\times10^3(-0.07)$$

$= -8400 - 5600 = -14000J$

Heat absorbed, $dQ^{+} = dQ_1 + dQ_2 = 31600J$

Heat rejected, $dQ^{-} = dQ_3 + dQ_4 = -26000J$

$$\text{Efficiency} = \frac{\text{Total work done}}{\text{Total heat absorbed}} = \frac{5600}{31600} = \frac{14}{79}$$

Problem: When a system is taken from the state A to the state B along the path ACB, 80 Joules of heat flows into the system and the system does 30 Joules of work.

(i) How much heat flows into the system along the path ADB if work done is 10 J?

(ii) The system is returned from state B to state A along the curved path. The work done on the system is 20 joule. Does the system absorb or liberate heat and how much?

(iii) If $U_A = 0$, $U_D = 40$ J. Find the heat absorbed in the process AD & DB

Soln. Along the path ACB,

$$\Delta U = \Delta Q - \Delta W \Rightarrow \quad U_B - U_A = 80 - 30 = 50$$

(i) Along the path ACD,

$$\Delta Q = \Delta U + \Delta W = (U_B - U_A) + \Delta W \qquad [\because \text{ internal energy is a state function}]$$

$= 50 + 10 = 60$ J

(ii) Along the curved path from B to A,

$$\Delta Q = \Delta U + \Delta W = (U_A - U_B) + \Delta W = (-50) + (-20) = -70 \text{ J}$$

So, liberated heat is 70 J

(iii) Given: $U_A = 0, U_0 = 40J$

Since, $U_B - U_A = 50 \Rightarrow U_B = 50J$

Now, for the path DB, $\Delta W = P\Delta V = 0$

So, $\Delta Q = \Delta U = U_B - U_D = 50 - 40 = 10\,J$

Now, for the path AD,

$$\Delta Q = \Delta U + \Delta W = (U_D - U_A) + \Delta W = (40 - 0) + 10 = 50\,J \qquad [\because \Delta W = 10\,J \text{ (Given)}]$$

Problem: A vessel contains an ideal monoatomic gas, which expands at constant pressure when heat Q is supplied to it. Then work done in the expansion is

(a) Q (b) $\frac{3}{5}Q$ (c) $\frac{2}{5}Q$ (d) $\frac{2}{3}Q$

Soln. The internal energy is

$$\Delta U = C_V dT = \frac{f}{2} R\,dT = \frac{3}{2} R\,dT = \frac{3}{2} P\,dV \qquad [\because \ PV = RT]$$

where $f = 3$ for monoatomic gas.

Now from first law of thermodynamic,

$$Q = \Delta U + PdV$$

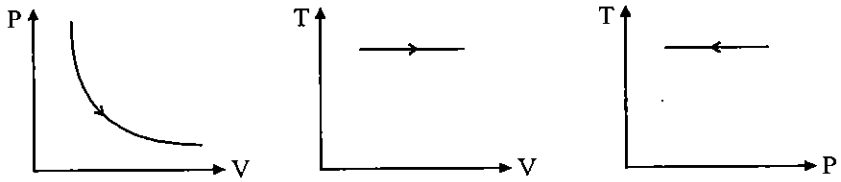
$$\Rightarrow \quad Q = \frac{3}{2} PdV + PdV \Rightarrow \quad PdV = \frac{2}{5} Q \Rightarrow \quad W = \frac{2}{5} Q$$

Correct option is (c)

Application of First Law of Thermodynamics

(1) Isothermal Process $(\Delta T = 0)$:

- It is the process in which the temperature of the system is kept fixed throughout.
- E.g. (i) Melting of ice at melting point
  (ii) Vaporization of water at 100°C.
- Ideal gas equation PV = constant ... (22)
- The graphs are



- First Law of Thermodynamics says

$\Rightarrow dQ = dU + dW = C_v\, dT + dW$ ... (23)

where $dU = C_v\, dT$ ... (24)

Since $dT = 0$, $dQ = dW$

$\Rightarrow$ All heat supplied to the system gets converted into the work.

- Work done

$$W = \int_{V_1}^{V_2} P\, dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$\Rightarrow \quad W = nRT\, \ell n \frac{V_2}{V_1} \qquad \text{... (25)}$$

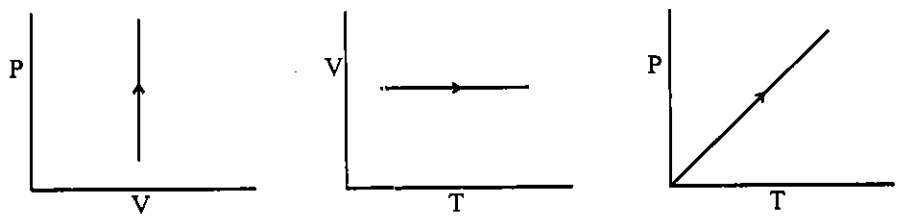
or $$\boxed{W = nRT\, \ell n \left(\frac{P_1}{P_2}\right)} \qquad \text{... (26)}$$

- Iso thermal process are generally slow.

CAREER ENDEAVOUR

(2) Isochoric process $(\Delta V = 0)$:

- It is the process in which volume remains constant.
- Ideal gas equation $\Rightarrow \frac{P}{T}$ = constant.
- The graphs are



- First law of thermodynamics gives $dQ = dU + PdV$

Since $dV = 0$,

$$\Rightarrow \quad dQ = dU = C_v dT \qquad \left[\because \; C_v = = \left(\frac{dQ}{dT}\right)_v\right] \qquad \text{... (27)}$$

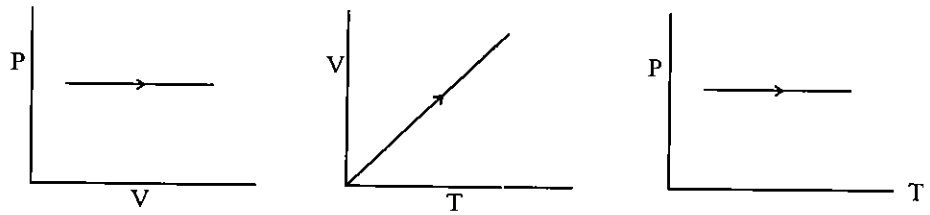
$\Rightarrow$ All heat given to the system is converted to the increase in internal energy.

- Work done

$$\boxed{W = \int_{V_1}^{V_2} PdV = 0} \quad \text{... (28)}$$

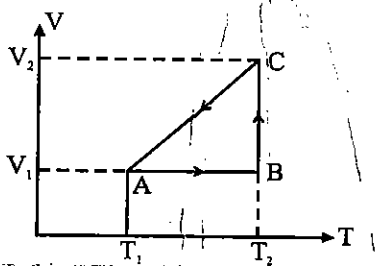
(3) Isobaric Process $(\Delta P = 0)$:

- It is the process for which pressure of the gas remains constant.
- Ideal gas equation $\Rightarrow$ $V \propto T$ or $\frac{V}{T} = \text{constant}$ ... (29)
- The graphs are



- First law of thermodynamics says $dQ = dU + PdV$ ... (30)
  where $dQ = C_P dT$ ... (31)
- Work done, $W = \int PdV = P\int_{V_1}^{V_2} dV = P(V_2 - V_1)$

Problem: Figure shows a process ABCA performed on an ideal gas. The net heat given to the system during the process is



(a) $R\left[T_2 \ln\left(\frac{V_1}{V_2}\right) + (T_1 - T_2)\right]$ (b) $R\left[T_2 \ln\left(\frac{V_1}{V_2}\right) + (T_2 - T_1)\right]$

(c) $R\left[T_2 \ln\left(\frac{V_2}{V_1}\right) + (T_1 - T_2)\right]$ (d) $R\left[T_2 \ln\left(\frac{V_2}{V_1}\right) + (T_2 - T_1)\right]$

In. Since change in internal energy in a cyclic process is zero, the net heat given to the system is the total work.

i.e. $\Delta Q = \Delta W$

$$\Rightarrow \quad \Delta Q = \underset{\text{(isochoric process)}}{W_{A\to B}} + \underset{\text{(isothermal process)}}{W_{B\to C}} + \underset{\text{(isobaric process)}}{W_{C\to A}}$$

$$= 0 + RT_2 \ell n\left(\frac{V_2}{V_1}\right) + P(V_2 - V_1)$$

$$= RT_2 \ell n\left(\frac{V_2}{V_1}\right) + R(T_2 - T_1) = R\left[T_2 \ell n\left(\frac{V_2}{V_1}\right) + (T_2 - T_1)\right]$$

Correct option is (d).

(4) Adiabatic Process $(\Delta Q = 0)$:

- When a gas expands or contracts without exchanging heat with the surrounding, the process is called *adiabatic process*.
- For this process, the system is insulated from the surrounding.
- Mathematically,

$$\Delta Q = 0 \qquad \ldots (32)$$

Equation govering is

$$PV^{\gamma} = \text{Constant} \quad \text{(for ideal gas)} \qquad \ldots (33)$$

Also, $\frac{nRT}{V} \cdot V^{\gamma} = \text{Constant} \quad (\because \ PV = nRT)$

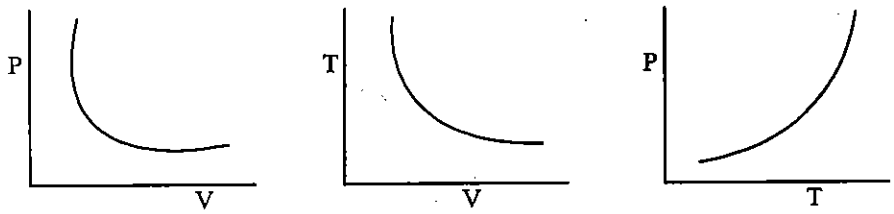
$$\Rightarrow \quad TV^{\gamma-1} = \text{Constant} \qquad \ldots (34)$$

Also, from equation (33), $P\left(\frac{nRT}{P}\right)^{\gamma} = \text{Constant}$

$$\Rightarrow \quad P^{1-\gamma}\, T^{\gamma} = \text{Constant} \qquad \ldots (35)$$

$$\text{where } \gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}$$

- The graphs are



- First Law of Thermodynamics : $dQ = dU + dW$

Since $dQ = 0, \ dW = -dU$

$\Rightarrow$ The workdone by the gas is at the expense of its internal energy.

- Work done

$$W = \int_{V_1}^{V_2} \frac{K}{V^{\gamma}} dV = \frac{K\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]}{1-\gamma} = \frac{KV_2^{1-\gamma} - KV_1^{1-\gamma}}{1-\gamma}$$

where $K = P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$=constant of proportionality

$$\therefore \ W = \frac{P_2 V_2^{\gamma} \cdot V_2^{1-\gamma} - P_1 V_1^{\gamma} V_1^{1-\gamma}}{1-\gamma}$$

$$\Rightarrow \ W = \frac{P_2 V_2 - P_1 V_1}{1-\gamma} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

Or $\boxed{W = \frac{nR}{\gamma - 1}(T_1 - T_2)}$

- Adiabatic process are generally very fast e.g. the bursting of a tyre.

Problem: A motor car tyre has a pressure of 2 atomsphere at room temperature 27°C. If the tyre suddenly bursts, find the resulting temperature.

Soln. $P_1 = 2$ atomsphere $\quad P_2 = 1$ atomsphere

$T_1 = 27°C = 27 + 273 = 300$ K $\quad T_2 = ?$ $\quad \gamma = 1.4$ for air

Using, $\dfrac{P_1^{\gamma-1}}{T_1^{\gamma}} = \dfrac{P_2^{\gamma-1}}{T_2^{\gamma}}$

$$\Rightarrow \left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$\Rightarrow \left(\frac{1}{2}\right)^{1.4-1} = \left(\frac{T_2}{300}\right)^{1.4} \qquad \Rightarrow \left(\frac{1}{2}\right)^{0.4} = \left(\frac{T_2}{300}\right)^{1.4}$$

Taking log both side,

$-0.4 \log 0.5 = 1.4 \log T_2 - 1.4 \log 300$

$\Rightarrow \quad -0.1204 = 1.4 \log T_2 - 3.4680$

$\Rightarrow \quad 1.4 \log T_2 = 3.4680 - 0.1204 = 3.3476$

$\Rightarrow \quad \log T_2 = 3.3476/1.4 = 2.3911$

$\Rightarrow \quad T_2 = 246.1$ K $= -26.9°C$

Problem: A quantity of air at 27°C and atmospheric pressure is suddenly compressed to half its original volume. Find the (i) pressure and (ii) temperature.

Soln. Given $P_1 = 1$ atm, $P_2 = ?$, $\gamma = 1.4$

$V_1 = V$, $V_2 = V/2$, $T_1 = 27°C = 300K$, $T_2 = ?$

For an adiabatic process, $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$$\Rightarrow \quad P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma} = 1\left(\frac{V}{\frac{V}{2}}\right) = 1(2)^{1.4} = 2.636\ atm$$

Also, $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$\Rightarrow \quad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 300\left(\frac{V}{\frac{V}{2}}\right)^{1.4-1} = 300(2)^{0.4} = 395.9K = 122.9°C$$

Problem: Air is compressed adiabatically of half its volume. Calculate the change in its temperature.

Soln. Let the initial temperature be T_1K and final temperature T_2K

Initial volume $V_1 = V$ and final volume $V_2 = \dfrac{V}{2}$

For adiabatic process, $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$\Rightarrow \quad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad or \quad T_2 = T_1(2)^{1.4-1}$$

$$\Rightarrow \quad T_2 = (2)^{0.4}T_1 = 1.319T_1$$

So change in temperture is

$$T_2 - T_1 = 1.319T_1 - T_1 = 0.319T_1 K$$

Problem: 1 gm molecule of a manoatomic $\left(\gamma = \frac{5}{3}\right)$ perfect gas at 27°C adiabatically compressed in reversible process from an initial pressure 1 atmosphere to a final pressure of 50 atmosphere. Calculate the resulting difference in temperature.

Soln. Given: $P = 1$ atm, $P_2 = 50$ atm, $T_1 = 27°C = 300K$, $T_2 = ?\ \gamma = \frac{5}{3}$

Using $\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}}$ *or* $\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$

$$\Rightarrow \quad (50)^{\frac{5}{3}-1} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}} \Rightarrow 50^{\frac{2}{3}} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}}$$

$$\Rightarrow \quad \frac{2}{3}\log 50 = \frac{5}{3}\log T_2 - \frac{5}{3}\log 300$$

$$\Rightarrow \quad T_2 = 1434\ K = 1161^{o} C$$

Problem: If the equation of state for a gas with internal energy U is $PV = \frac{1}{3}U$ then the equation for an adiabatic process is:

(a) $PV^{1/3} = \text{constant}$ (b) $PV^{2/3} = \text{constant}$ (c) $PV^{4/3} = \text{constant}$ (d) $PV^{3/5} = \text{constant}$

Soln. For adiabatic process,

$$dQ = 0$$

$$\Rightarrow \quad dU = -dW = -PdV$$

But $\quad PV = \frac{1}{3}U \Rightarrow U = 3PV$

$$\Rightarrow \quad d(3PV) = -PdV \Rightarrow 3\,PdV + 3\,VdP = -PdV$$

$$\Rightarrow \quad 3\,VdP = -4PdV \quad \text{or} \quad \frac{dP}{P} = -\frac{4}{3}\frac{dV}{V}$$

Integrating, $\log P = -\frac{4}{3}\log V + \text{constant} \Rightarrow \log PV^{4/3} = \text{constant}$

$$\Rightarrow \quad \text{or} \quad PV^{4/3} = \text{constant}$$

Hence, correct option is (c).

Problem: An ideal gas expands adiabatically but quasistatically from state $i(P_i V_i T_i)$ to a state $f(P_f V_f T_f)$. What is the change in its internal energy?
What would this change be if the expansion were isothermally?

Soln. If the process is performed in such a way that at any instant during the process the system is very nearly in the thermodynamic equilibrium, the process is called *quasistastic,* this means we can specify pressure, volume, temperature uniquely at any instant during such a process. Thus a quasistastic process is an idealised process in which all changes take place infinitely slowly.

From first law $dQ = dU + dW$
But for adiabatic process $dQ = 0$
So $dU = -dW$

Total change in internal energy $= \int_i^f dU = -\int_i^f PdV = -\int_i^f \frac{K}{V^\gamma} dV$

So $U_f - U_i = -K\left(\frac{V^{-\gamma+1}}{-\gamma+1}\right)_i^f \qquad \left(\because PV^\gamma = K \Rightarrow P = \frac{K}{V^\gamma}\right)$

$= \frac{K}{1-\gamma}\left(V^{-\gamma+1}\right)_i^f$

But $P_iV_i^\gamma = P_fV_f^\gamma = K$

So $U_f - U_i = \frac{1}{1-\gamma}\left(P_fV_f^\gamma\, V_f^{-\gamma+1} - P_iV_i^\gamma\, V_i^{-\gamma+1}\right)$

$= \frac{1}{1-\gamma}\left(P_fV_f - P_iV_i\right) \left(\because PV = nRT\right) = \frac{nR}{1-\gamma}\left(T_f - T_i\right)$

(ii) for isothermal expansion $T_i = T_f$

$$U_f - U_i = \frac{f}{2}nR\left(T_f - T_i\right) = 0$$

So for adiabatic isothermal process, the change in internal energy is zero.

Problem: A monoatomic ideal gas, initially at temperature T_1, is enclosed in a cylinder fitted with a frictionless piston. The gas is allowed to expand adiabatically to a temperature T_2 by releasing the piston suddenly. If L_1 and L_2 are the lengths of the gas column before and after expansion respectively, then T_1/T_2 is given by

(a) $(L_1/L_2)^{2/3}$ (b) (L_1/L_2) (c) L_2/L_1 (d) $(L_2/L_1)^{2/3}$ **[IIT-JEE : 2000]**

Soln. During adiabatic expansion, we know

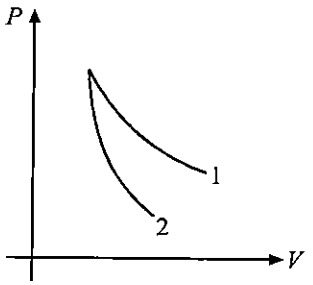
$TV^{\gamma-1} = \text{constant}$ or $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

For a monoatomic gas, $\gamma = \frac{5}{3}$

$\therefore \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{AL_2}{AL_1}\right)^{(5/3)-1}$ (A = Area of cross-section of piston)

$= \left(\frac{L_2}{L_1}\right)^{2/3}$

Problem: P-V plots for two gases during adiabatic processes are shown in the figure. Plots 1 and 2 should correspond respectively to



(a) He and O_2 (b) O_2 and He (c) He and Ar (d) O_2 and N_2

[IIT-JEE : 2001]

Soln. In adiabatic process, $PV^{\gamma} = \text{constant}$

Therefore, slope of P-V graph, $\frac{dP}{dV} = -\gamma\frac{P}{V}$

$\Rightarrow$ slope $\propto \gamma$ (with negative sign)

From the given graph, $(\text{slope})_2 > (\text{slope})_1$

$\therefore \gamma_2 > \gamma_1$

Therefore, 1 should correspond to O_2 ($\gamma = 1.4$) and 2 should correspond to He ($\gamma = 1.67$).

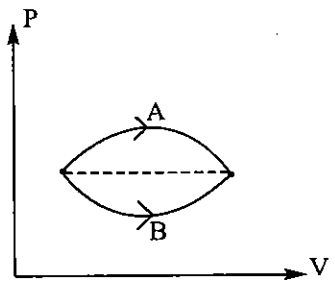
Hence, correct option is (b)

(5) Cyclic Process

- In a *cyclic process*, the system returns to its intial state.
- Since internal energy is a state function, $\Delta U = 0$
- First Law of Thermodynamics $\Rightarrow$ $\Delta Q = \Delta U + \Delta W$ $\Rightarrow$ $\Delta Q = \Delta W$

Problem: Figure shows the process A and B on a system. Let ΔQ_1 and ΔQ_2 be the heat given to the system in the process A and B respectively then

(a) $\Delta Q_1 > \Delta Q_2$ (b) $\Delta Q_1 = \Delta Q_2$ (c) ΔW (d) $\Delta Q_1 \leq \Delta Q_2$



Soln. Since ΔU is same for both the process and ΔW is the amount of work which is represented by the area under the curve and since area under A is greater than area under B.

$\Delta W_1 > \Delta W_2 \Rightarrow \Delta W_1 + \Delta U > \Delta W_2 + \Delta U$

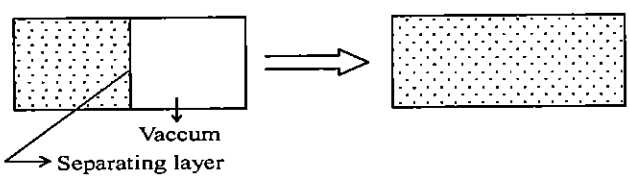
So $\Delta Q_1 > \Delta Q_2$

If both the arrow signs are changed then $\Delta Q_1 < \Delta Q_2$

(6) Free expansion

- In a system say if a gas expands in such a way that no heat enters or leave the system (adiabatic process) and also no work is done by or on the system, the gas is said to be expanded freely.
- For free expansion, $dQ = 0$ and $dW = PdV = 0$
  (There is no pressure acting on the gas during free expansion)
- First Law of Thermodynamics $\Rightarrow$ $dU = 0$

e.g. If initially the gas is contained in half of the box and the other half has vacuum in it. When the separating layer is suddenly removed, the gas expands freely in the whole box.



Problem: The internal energy of n moles of a gas is given by $E = \frac{3}{2}nRT - \frac{a}{v}$ where V is the volume of the gas at temperature T and a is a positive constant. One mole of the gas in state (T_1, V_1) is allowed to expand adiabatically into vacuum to a final state (T_2, V_2). The temperature T_2 is:

(a) $T_1 + \frac{a}{R}\left(\frac{1}{V_2} + \frac{1}{V_1}\right)$ (b) $T_1 - \frac{2}{3}\frac{a}{R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$

(c) $T_1 + \frac{2}{3}\frac{a}{R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$ (d) $T_1 - \frac{1}{3}\frac{a}{R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$

oln. Since the process is free expansion process. So the change in internal energy for free expansion process is zero.

$$\Rightarrow \quad U_2 - U_1 = 0$$

$$\Rightarrow \quad \frac{3}{2}nRT_1 - \frac{a}{V_1} = \frac{3}{2}nRT_2 - \frac{a}{V_2}$$

$$\Rightarrow \quad \frac{3}{2}nRT_2 = \frac{3}{2}nRT_1 - \frac{a}{V_1} + \frac{a}{V_2} = \frac{3}{2}nRT_1 + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

For $n = 1$,

$$\Rightarrow \quad \boxed{T_2 = T_1 + \frac{2a}{3R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$

Hence correct option is (c).

Problem: Two gases separated by a impermeable but movable partition are allowed to freely exchange energy. At equilibrium, the two sides will have the same

(a) pressure and temperature (b) volume and temperature

(c) pressure and volume (d) volume and energy

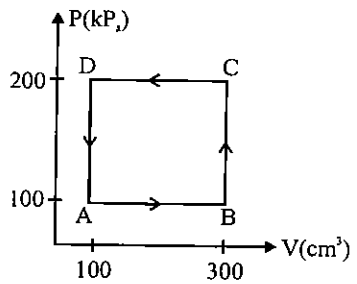
ln. Once the system is released freely, due to exchange of energy both sides will attain thermal equilibrium by attaining the same temperature. Also, due to unbalanced pressure, both the sides will attain mechanical equilibrium by balancing the pressure on both sides of the movable wall.

Hence correct option is (a).

Problem: A thermodynamic system is taken through the cycle *ABCD* as shown in figure

(i) Calculate the work done by the gas (system) during the path *AB*, *BC*, *CD*, *DA*

(ii) Find the total heat rejected by the gas during the process *ABCDA*.



n. (i) $W_1 = PdV = 100\ kPa \times 200\ cm^3$ (along *AB*)

$$= 100 \times 1000 \times \frac{200}{10^6} \frac{Pa}{m^3} = 20\ J$$

$W_2 = 0$ because the change in volume is zero. (along BC)

$W_3 = -P \times dV = -200\ kPa \times 200\ cm^3$ (along CD)

$$= -200 \times 1000 \times \frac{200}{10^6} \frac{Pa}{m^3}$$

$$= -40\ J$$

The negative sign is due to decrease in volume

$W_4 = 0$ because the change in volume is zero. (along DA)

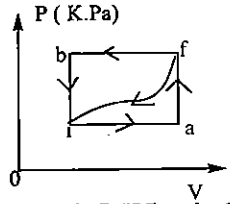
$\therefore\ W = W_1 + W_2 + W_3 + W_4 = 20 - 40 = -20J$

(ii) $dQ = dU + dW$

For cyclic process $dU = 0$

$dQ = dW = -20J \Rightarrow$ Heat rejected by the gas

Problem: When a system is taken from a state i to f along the path iaf as shown in figure. It is found that heat Q absorbed by the system is 50 cal and the work done by the system is 20 cal. Along the path ibf $Q = 36$ cal.



(i) what is the work done along the path ibf?

(ii) If the work done on the system is equal to 13 cal for the curved returned path fi. What is the value Q for this path?

(iii) If internal energy of the system in initial state is equal to 10 cal. What is the internal energy of the system in final state ?

(iv) If internal energy of the system for state b = 22 cal. What are the values Q for the process bf and ib?

Soln. Given $U_i = 10$ cal, $Q = 50$ cal and $W = 20$ cal

for the path iaf,

(i) $Q = U_f - U_i + W$

$\Rightarrow\ 50 = U_f - 10 + 20$

$\Rightarrow\ \boxed{U_f = 40\ cal}$

So work done along path ibf,

As $dQ = 36$

$dQ = dU + dW$

$\Rightarrow\ dW = dQ - dU = 36 - (40 - 10) = 6$ cal

(ii) $W = 13$ cal for ($f \rightarrow$ i)

$W = -13$ cal

$dQ = dU + dW$

$= (U_i - U_f) - 13 = -30 - 13 = -43$ Cal

(iii) $\Delta U = 30 \Rightarrow U_f - U_i = 30$

$\Rightarrow U_f - 10 = 30 \Rightarrow U_f = 40$

(iv) $U_b = 22$ cal, $U_f = 40$ cal

So for path $bf \Rightarrow U_f - U_b = 18$ cal

As $\Delta W = 6 \quad \{\because i \to b, \Delta W = 0\}$

$dQ = 18 + 6 = 24\ cal$

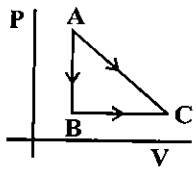
For bath $i \to b$

$U_b = 22\ cal \quad U_i = 10\ cal$

$\Delta U = 12\ cal, \quad \Delta W = 0, \quad \Delta Q = \Delta U + \Delta W$

$\Rightarrow \quad \Delta Q = 12\ cal$

Problem: A given quantity of gas is taken from the state $A \to C$ reversibly, by two paths, $A \to C$ directly and $A \to B \to C$ as shown in the figure below.



During the $A \to C$ the work done by the gas is 100 J and the heat absorbed is 150 J. If during the process $A \to B \to C$ the work done by the gas is 30 J, the heat absorbed is:

(a) 20J (b) 80J (c) 220 J (d) 280 J

Soln. Using $dQ = dU + dW_1$

For path AC: $150\ J = dU + 100\ J$

$\Rightarrow dU = 150\ J - 100J = 50\ J$

For path ABC: $dQ = dU + dW_2 = 50J + 30J = 80J$ $(\because$ internal energy is a state function$)$

Correct option is (b)

Problem: Figure shows a process $ABCA$ performed on an ideal gas. Find the net heat given to the system during the process.

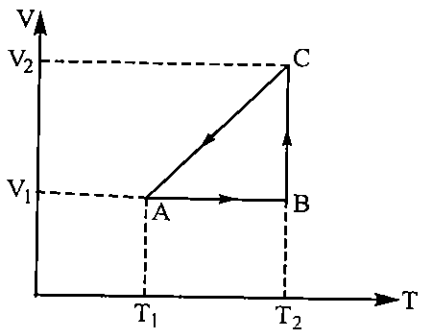
Soln. Since the process is cyclic so the change in internal energy $dU = 0$

Since $dU = 0 \quad \Rightarrow \quad dQ = dW = PdV$

For the process AB change in volume = Zero

$\Rightarrow W_1 = 0$

For process BC, temperature is constant



$$W_2 = \int_{V_1}^{V_2} dW_2 = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{TR}{V} dV$$

$$W_2 = RT\left[\ell n\, V\right]_{V_1}^{V_2} = RT_2 \ell n \frac{V_2}{V_1}$$

For process $CA, \frac{V}{T} = \text{constant}$

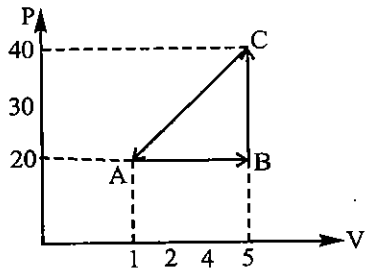
Also, $PV = RT \Rightarrow \frac{V}{T} = \frac{R}{P} \Rightarrow V = \frac{RT}{P} \Rightarrow dV = \frac{R}{P}dT$

$$W_3 = \int_{T_2}^{T_1} dW = \int_{T_2}^{T_1} PdV = \int_{T_2}^{T_1} P\frac{R}{P}dT = [RT]_{T_2}^{T_1} = R(T_1 - T_2)$$

$$W_3 = R(T_1 - T_2)$$

Now, $Q = W = W_1 + W_2 + W_3 = R\left[T_2 \ell n \frac{V_2}{V_1} + (T_1 - T_2)\right]$

Problem: A gas is carried through a cycle $ABCA$ as shown in the P–V diagram. Determine weather the heat is given to the system or by the system, work is done by the system or on the system, internal energy of the system increases or decreases in the following process.



(a) For the process AB if $\Delta U = +\text{Ve}$ (b) for the process BC if $Q = +\text{Ve}$

(c) For process CA (d) Net work done in the complete cycle.

Soln. (i) $\Delta U = +Ve$ (given) $\Rightarrow$ so internal energy of the system increase

$\Delta W = +Ve$ (work done by the system because volume increase)

$\Delta Q = \Delta U + \Delta W = +Ve$ (Heat given to the system)

(ii) For BC

$Q = +Ve$ (given) $\Rightarrow$ Heat given to the system

$\Delta W = 0$ ($W = PdV$ and V is constant)

$\Delta U = +Ve$ $\Delta Q = \Delta U + \Delta W$. Internal energy of the system increase)

(iii) For process CA

For process ABC ΔU = positive $\left(\because (\Delta U)_{AC} = (\Delta U)_{AB} + (\Delta U)_{BC} = (+Ve) + (+Ve)\right.$

For CA Process $(\Delta U)_{CA} = -(\Delta U)_{AC}$ = negative

$(\Delta U)_{CA} = -ve$ (Internal energy of the system decrease)

$\Delta W = -ve$ ($\because$ volume decrease so work done on the system)

$\Delta Q = -ve\,(\Delta Q = \Delta U + \Delta W = -ve$, heat is given by the system)

(iv) Net workdone in complete cycle = area under the curve

$$= \frac{1}{2} \times AB \times BC = \frac{1}{2} \times 4 \times 20 = 40\ Joule.$$

Slope of Adiabatic and Isothermal Process

(a) Isothermal Process :

$$PV = \text{constant} \Rightarrow PdV + VdP = 0 \Rightarrow \left(\frac{dP}{dV}\right)_{iso} = -\frac{P}{V}$$

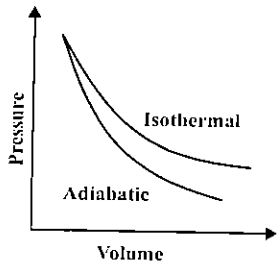
(b) Adiabatic Process :

$$PV^{\gamma} = \text{Constant} \Rightarrow P\gamma V^{\gamma-1}dV + dP \cdot V^{\gamma} = 0 \Rightarrow \frac{dP}{dV} = -\frac{PV^{\gamma-1}\gamma}{V^{\gamma}}$$

$$\Rightarrow \left(\frac{dP}{dV}\right)_{adia} = -\gamma\frac{P}{V}$$

$$\therefore \quad \boxed{\frac{(dP/dV)_{adia.}}{(dP/dV)_{iso.}} = \gamma > 1}$$

(Slope of adiabatic is γ-times than that of isothermal).



Bulk Modulus or Incompressibility

The *bulk modulus* or *incompressibility* of a substance is a measure of how incompressible/resistant to compressibility that substance is. It is defined as the ratio of the infinitesimal pressure increase to the resulting relative decrease of the volume.

Mathematically, $K = -V\left(\frac{\partial P}{\partial V}\right)_T$

Isothermal Compressibility

In thermodynamics and fluid mechanics, *compressibility*, (also known as coefficient of compressibility or isothermal compressibility) is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change.

Mathematically, $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Coefficient of Volume Expansion

It is a measure of how easily a substance expands on increasing its temperature. It is defined as the ratio of the infinitesimally increase in the volume of the substance to the infinitesimally increase in the temperature per unit original volume.

Mathematically, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Problem: For a gas under isothermal conditions, its pressure P varies with volume V as $P \propto V^{-5/3}$. The bulk modulus B is proportional to

(a) $V^{-1.2}$ (b) $V^{-2.3}$ (c) $V^{-3.5}$ (d) $V^{-5/3}$

In. According to ideal gas equation, we get $PV = nRT$. For isothermal condition, we get $dPV + PdV = 0$.

$$\Rightarrow \quad P = -\frac{dP}{dV/V} = B$$

So, $P = B$ ...(i)

But given that $P \propto V^{-5/3}$ ...(ii)

Comparing equations (i) and (ii), we get $B \propto V^{-5/3}$.

Hence correct option is (d).

Problem: The isothermal compressibility, κ of an ideal gas at temperature T_0 and volume V_0, is given by

(a) $-\frac{1}{V_0}\frac{\partial V}{\partial P}\Big|_{T_0}$ (b) $\frac{1}{V_0}\frac{\partial V}{\partial P}\Big|_{T_0}$ (c) $-V_0\frac{\partial P}{\partial V}\Big|_{T_0}$ (d) $V_0\frac{\partial P}{\partial V}\Big|_{T_0}$

Soln. Isothermal incompressibility is defined as $-\frac{\partial P}{\partial V/V_0}\Big|_{T_0}$

Hence correct option is (a).

Problem: Express the isothermal compressibility $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ of one mole of vander Waal's gas as a function of temperature and volume.

Soln. Isothermal compressibility is defined as

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{(for one mole)}$$

The vander Waal gas equation, is

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT$$

$$\Rightarrow \quad P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\therefore \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\therefore \quad \beta = -\frac{1}{V}\left(\frac{\partial P}{\partial V}\right)_T = \frac{-1}{V\left[\frac{RT}{(V-b)^2} + \frac{2a}{V^3}\right]} \Rightarrow \boxed{\beta = \frac{1}{\frac{RTV}{(V-b)^2} - \frac{2a}{V^2}}}$$

PROBLEMS TO BE PLAYED

1. The change in the internal energy of the gas is directly proportional to–
(a) The change in volume (b) Change in pressure
(c) Change in temperature (d) None of these

2. The first law of thermodynamics is conservation of–
(a) Momentum (b) Energy (c) Both (a) and (b) (d) None of these

3. A thermos bottle containing coffee is vigorously shaken and thereby the temperature of coffee rises. Considering the coffee as the system, which of the following is ***CORRECT***.
(a) $Q = 0$; $W = -$ve; $dU = +$ ve (b) $Q = 0$; $W = +$ ve; $dU = +$ ve
(c) $Q = 0$; $W = -$ve; $dU = -$ve (d) $Q = 0$; $W = +$ ve; $dU = -$ ve

4. A resistor immersed in running water carries an electric current. Consider the resistor as the system–
(a) $Q = 0$; $W = -$ve; $dU = -$ve (b) $Q = 0$; $W = -$ve; $dU = +$ ve
(c) $Q = 0$; $W = +$ ve; $dU = -$ve (d) $Q = 0$; $W = +$ ve; $dU = +$ ve

5. The quantity remaining constant in the isothermal expansion of an ideal gas is–
(a) Heat (b) Internal energy
(c) Pressure (d) Temperature and pressure

6. The work done W during an isothermal process in which the gas expands from an initial volume V_1 to a final voluem V_2 is given by–
(R = Gas constant, T = Temperature)

(a) $R(V_2 - V_1)\log_e\left(\frac{T_1}{V_2}\right)$ (b) $(T_2 - T_1)\log_e\left(\frac{V_2}{V_1}\right)$

(c) $RT\log_e\left(\frac{V_2}{V_1}\right)$ (d) $RT\log_e\left(\frac{V_1}{V_2}\right)$

7. If a system A is in thermal equilibrium separately with B and C, then B and C are also in thermal equilibrium with each other. This is the statement of–
(a) Zeroth law of thermodynamics (b) First law of thermodynamics
(c) Second law of thermodynamics (d) Third law of thermodynamics

8. In a cyclic process
(a) Work done is zero
(b) Work done by the system is equal to the quantity of heat given to the system
(c) Work done does not depend on the quantity of heat given to the system
(d) The internal energy of the system increases

CAREER ENDEAVOUR

9. One mole of a perfect gas expands adiabatically. As a result of this, its pressure, temperature and volume change from P_1, T_1, V_1 to P_2, T_2 and V_2 respectively. If molar specific heat at constant volume is C_V, then the work done by the gas is–

(a) $2.303\ P_1V_1\ \log\frac{V_2}{V_1}$ (b) $RT_1\log\frac{V_2}{V_1}$ (c) $\frac{P_1^2V_1^2 - P_2^2V_2^2}{R(T_2 - T_1)}$ (d) $C_V(T_2 - T_1)$

10. For a thermodynamic system work done in a process depends upon–
(a) The path (b) State of the system
(c) External pressure (d) Nature of the system

11. Work done in an isothermal change in a gas is

(a) $W = T\log_e\frac{V_2}{V_1}$ (b) $W = R\log_e\left(\frac{V_2}{V_1}\right)$

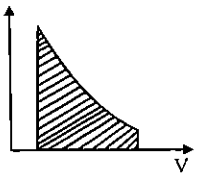
(c) $W = RT\log_{10}\left(\frac{V_1}{V_2}\right)$ (d) $W = RT\cdot\log_{10}\left(\frac{V_2}{V_1}\right)$

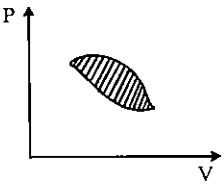
12. In an isobaric process work done is

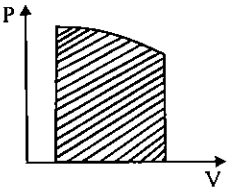
(a) $W = RT \log_e\left(\frac{V_2}{V_1}\right)$ (b) $W = \frac{R}{\gamma - 1}(T_1 - T_2)$

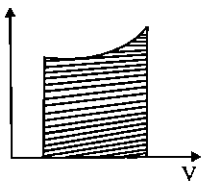
(c) $W = P(V_2 - V_1)$ (d) $W = 0$

13. The work done by a gas in adiabatic expansion is represented by the diagram–

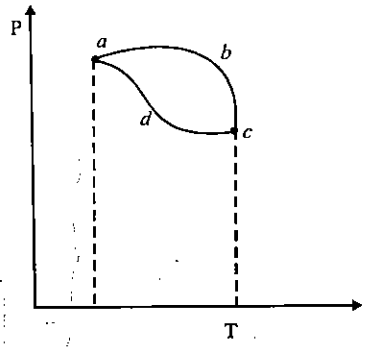
(a) 

(b) 

(c) 

(d) 

14. In the *PV* diagram below which is the correct statement?

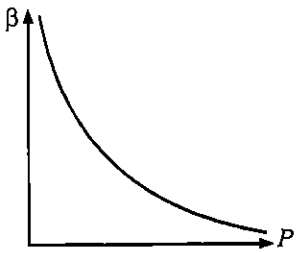


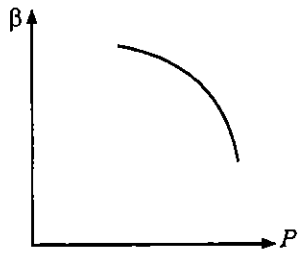
(a) Any point on the line *abc* represents a higher temperature than any point on the line *adc*
(b) The area *abcda* represents the work done by the system for the process
(c) Heat is lost to the surroundings during the process is represented by path *adc*
(d) The path *abc* and *adc* represents isothermals

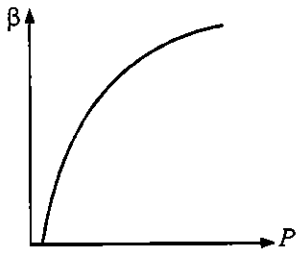
15. In an isothermal change the internal energy of molecules–

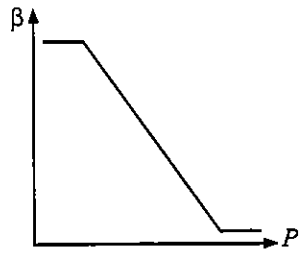
(a) May increase or decrease (b) Does not change
(c) Increases (d) Decreases

16. Which of the following graph correctly represent the variation of $\beta = -\frac{dV/dP}{V}$ with P for an ideal gas at constant temperature ?

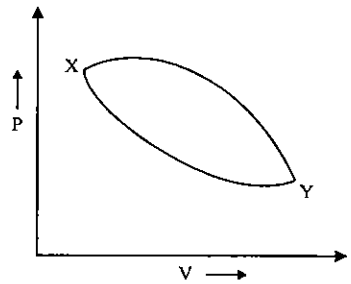
(a) 

(b) 

(c) 

(d) 

17. A piston containing an ideal gas is originally in the state X (see fig.). The gas is taken through a thermal cycle $X \rightarrow Y \rightarrow X$ as shown. They work done by the gas is positive if the direction of the thermal cycle is



(a) Clockwise (b) Counter clockwise
(c) Neither clockwise nor counter clockwise
(d) Clockwise from $X \rightarrow Y$ and counter clockwise from $Y \rightarrow X$

18. An ideal gas in a cylinder is compressed adiabatically to one-third of its initial volume. During this process 20J work is done on the gas by compressing agent. Which of the following statements is true for this case?
(a) Change in the internal energy in this process is zero
(b) The internal energy increases by 20 J
(c) The internal energy decreases by 20 J
(d) Temperature of the gas decreases

19. The relation connecting pressure and volume in an adiabatic expansion is given by PV^n = constant. If the specific heat at constant pressure is l and the specific heat at constant volume is m, then n is given by–

(a) $\frac{m}{l}$ (b) $\frac{l}{m}$ (c) $l-m$ (d) $m-l$

20. The internal energy of a system is the
(a) potential energy of the particle of the system
(b) kinetic energy of the particle of the system
(c) sum of kinetic and mutual potential energies of the particles of the system
(d) difference between the kinetic and mutual potential energies of the system

21. A vessel contains an ideal monoatomic gas, which expands at constant pressure when heat Q is supplied to it. Then work done in the expansion is

(a) Q (b) $\frac{3}{5}Q$ (c) $\frac{2}{5}Q$ (d) $\frac{2}{3}Q$

CAREER ENDEAVOUR

22. The slopes of isothermal and adiabatic curves are related as
(a) Isothermal curve slope = Adiabatic curve slope
(b) Isothermal curve slope = $\gamma \times$ Adiabatic curve slope
(c) Adiabatic curve slope = $\gamma \times$ Isothermal curve slope
(d) Adiabatic curve slope = $\frac{\gamma}{2} \times$ Isothermal curve slope

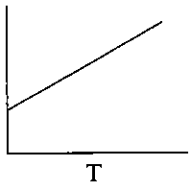
23. Two bodies are said to be in thermal equilibrium when they are equal in
(a) temperature (b) heat content
(c) heat capacity (d) specific heat

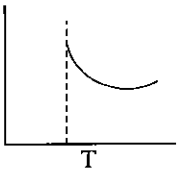
24. If the equation of state for a gas with internal energy U is $PV = \frac{1}{3}U$, then the equation for an adiabatic process is:

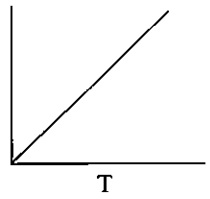
(a) $PV^{1/3}$ = constant (b) $PV^{2/3}$ = constant (c) $PV^{4/3}$ = constant (d) $PV^{5/3}$ = constant

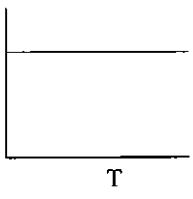
25. When a perfect gas is supposed to expand freely against vacuum in a insulated vessel, the gas has undergone–
(a) An increase in pressure (b) A change in temperature
(c) A change in entropy (d) A change in phase

26. A gas obey the equation of state $P(V-b) = RT$ where b is a constant. For this gas a plot of V versus T at constant P (isobar) will be–

(a) 

(b) 

(c) 

(d) 

27. The general gas equation $PV = RT$ was improved by Vander Waal who introduced a correction factor $\frac{a}{V^2}$ which is added to P. The term, $\frac{a}{V^2}$, relates to

(a) Volume of the molecules
(b) Effective area of the molecules
(c) Average velocity of the molecules
(d) Force of attraction between the molecules

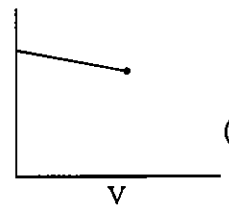
28. The pressure of a gas filled in a vessel is P, if the masses of all the molecules of the gas are halved and their speeds doubled, the new pressure will be–

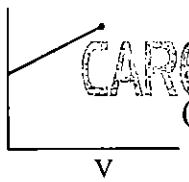
(a) $4P$ (b) $2P$ (c) P (d) $\frac{P}{2}$

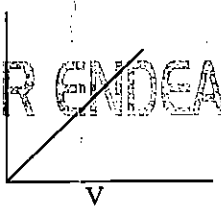
29. For a gas obeying Vander Waal's equation the critical constants can be related correctly by

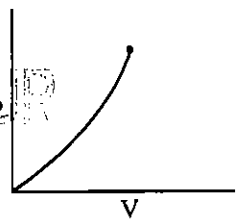
(a) $\frac{RT_c}{P_cV_c} = \frac{8}{3}$ (b) $\frac{P_cV_c}{RT_c} = \frac{3}{8}$ (c) $\frac{RT_c}{P_cV_c} = \frac{3}{8}$ (d) none of these

30. Which of the following graphs satisfy Boyle's Law?

(a) 

(b) 

(c) 

(d) 

CAREER ENDEAVOUR

31. On suffering adiabatic expansion the internal energy of a gas–
(a) Increases
(b) Decreases
(c) Remains unchanged
(d) May increase or decrease

ANSWER KEY

1. (c)	**2. (b)**	**3. (a)**	**4. (b)**	**5. (b)**	**6. (c)**	**7. (a)**
8. (b)	**9. (d)**	**10. (a)**	**11. (d)**	**12. (c)**	**13. (a)**	**14. (b)**
15. (b)	**16. (a)**	**17. (d)**	**18. (c)**	**19. (b)**	**20. (c)**	**21. (c)**
22. (c)	**23. (a)**	**24. (c)**	**25. (a)**	**26. (a)**	**27. (d)**	**28. (b)**
29. (a)	**30. (c)**	**31. (b)**				

Chapter 3

The Carnot Engine

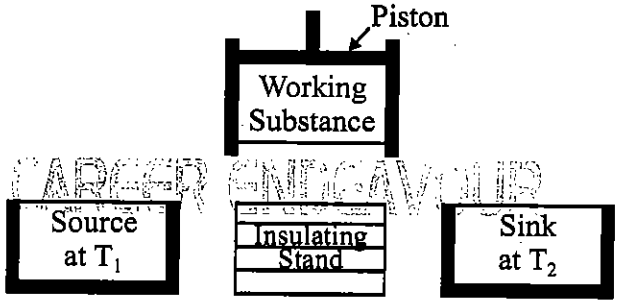
The Carnot Engine

Suppose we have a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2. What is the maximum efficiency possible for a heat engine operating between the two reservoir and what cycle of processes should be adopted to achieve the maximum efficiency ? Sadi Carnot, a French engineer first considered these questions in 1824.

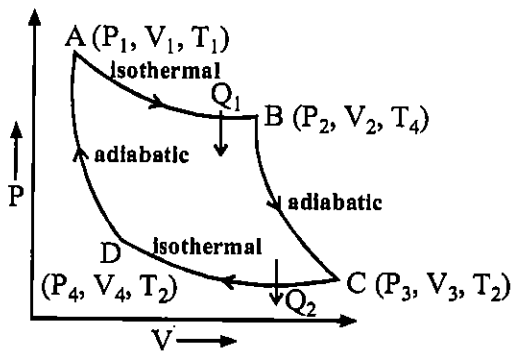
A *Carnot engine* governs by *Carnot cycle* which is defined as any cyclic process bounded by two reversible isothermals and two reversible adiabatics.

It consists of the following :

1. A cylinder fitted with piston
2. A source at higher temperature (T_1)
3. A source at lower temperature (T_2)
4. An insulating stand



The Carnot cycle is shown as :



The various steps in the Carnot engine are as follows :

(a) Step $A \rightarrow B$: Isothermal expansion of the gas.

Since the internal energy of an ideal gas is a function of its temperature only, the internal energy is constant in the isothermal process $A \rightarrow B$ and the heat flow Q_1 into the gas in this process is equal to the work done by the gas W_1. So we have

$$Q_1 = W_1 = nRT_1 \ln\left(\frac{V_2}{V_1}\right) \quad \ldots (1)$$

where V_1 and V_2 are the volumes in states A and B, respectively.

(b) Step $B \rightarrow C$: Adiabatic expansion of the gas.

To expand adiabatically, the gas needs to perform work W_2 which it does at the expense of its internal energy and hence fall in its temperature. So, we have

$$W_2 = nR\frac{(T_1 - T_2)}{\gamma - 1} \quad \ldots (2)$$

(c) Step $C \rightarrow D$: Isothermal compression of the gas.

The gas is compressed isothermally from the volume V_3 to V_4. This requires work W_3 need to be done on the gas. This is the amount of heat Q_2 released by the gas to the reservoir. This gives

$$Q_2 = W_3 = nRT_2 \ln\left(\frac{V_4}{V_3}\right) \quad \ldots (3)$$

(d) Step $D \rightarrow A$: Adiabatic compression of the gas.

The gas in the system is further compressed adiabatically. The necessary energy required to perform this task increases the internal energy of the gas resulting in the rise of temperature of the system. The work done involves in the process is given by

$$W_4 = nR\frac{(T_2 - T_1)}{\gamma - 1} \quad \ldots (4)$$

So the total workdone by the gas in one complete cycle is

$$W = W_1 + W_2 + W_3 + W_4$$

CAREER ENDEAVOUR

$$= nRT_1 \ln\left(\frac{V_2}{V_1}\right) + nR\frac{(T_1 - T_2)}{\gamma - 1} - nRT_2 \ln\left(\frac{V_4}{V_3}\right) - nR\frac{(T_2 - T_1)}{\gamma - 1}$$

$$= nRT_1 \ln\left(\frac{V_2}{V_1}\right) - nRT_2 \ln\left(\frac{V_4}{V_3}\right) \quad \ldots (5)$$

Now from equations (1) and (3),

$$\frac{Q_1}{Q_2} = \frac{nRT_1 \ln(V_2/V_1)}{nRT_2 \ln(V_4/V_3)} = \frac{T_1}{T_2}\frac{\ln(V_2/V_1)}{\ln(V_4/V_3)} \quad \ldots (6)$$

Since states B and C lie on the same adiabatic and hence

$$T_1 V_2^{\gamma - 1} = T_2 V_3^{\gamma - 1} \quad \ldots (7)$$

Similarly, since states A and D lie on the same adiabatic,

$$T_1 V_1^{\gamma - 1} = T_2 V_4^{\gamma - 1} \quad \ldots (8)$$

Now dividing equation (7) by (8), we have $\frac{V_2}{V_1} = \frac{V_3}{V_4}$ ... (9)

Now using equation (9) in (6), we get

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}\frac{\ln(V_3/V_4)}{\ln(V_4/V_3)} \quad \ldots (10)$$

$$\Rightarrow \frac{Q_1}{Q_2} = -\frac{T_1}{T_2} \text{ or } \frac{Q_2}{Q_1} = -\frac{T_2}{T_1} \quad \ldots (11)$$

So the magnitude is $\boxed{\frac{Q_2}{Q_1} = \frac{T_2}{T_1}}$ ... (12)

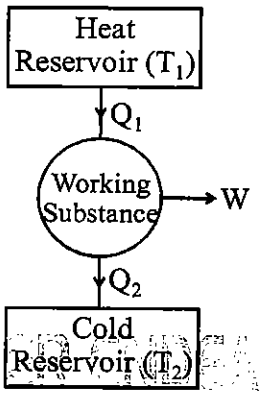
Thus for an "ideal gas", the ratio Q_2/Q_1 depends only on the temperature of the source (T_1) and of the sink (T_2) and independent of the nature of the working substance.

The Heat Engine

It is a device by which a system is made to undergo a cyclic process that results in conversion of heat to work. Since the process is cyclic, the net flow of heat Q into the gas or the system, in any complete cycle, is equal to the work W done by the engine per cycle.

i.e. $Q = W$ ... (13)

The Schematic representation of a heat engine is



Here Q_1 is the amount of heat given to the working substance from the hot reservoir at temperature T_1. A part of this Q_1 amount of heat is used to perform work W by the system and the rest of the heat Q_2 is rejected to the sink at temperature T_2. So by the conservation of energy

$$Q_1 = W + Q_2 \quad \ldots (14)$$

$$\Rightarrow W = Q_1 - Q_2 \quad \ldots (15)$$

The efficiency (η) is defined as $\eta = \frac{\text{what you get}}{\text{what you pay}}$.

For the heat engine, we have given Q_1 amount of heat to the system and as a result, it performs W amount of work. So the thermal efficiency is $\eta = \frac{W}{Q_1}$ ... (16)

$$\Rightarrow \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad \ldots (17) \quad \text{[Using (15)]}$$

$$\Rightarrow \boxed{\eta = 1 - \frac{T_2}{T_1}} \quad \text{... (18)} \quad \text{[Using (12)]}$$

The definition in equation (17) is valid for every type of heat engine whereas equation (18) is valid only when the working substance is an ideal gas.

Clearly, the efficiency of a heat engine depends only on the temperatures of the source (T_1) and of the sink (T_2) and independent of the nature of the working substance.

For $Q_2 = 0$ i.e., if no heat gets wasted, the efficiency of the heat engine is 1 or 100 %. It means that all the heat given to the system is utilized in the work. This is an ideal case and is not practically possible.

Moreover, the value of 'η' lies between 0 and 1.

Problem: Find the efficiency of the Carnot engine working between the steam point and the ice point.

Soln. Given $T_1 = 100°C = 100 + 273 = 373$ K (steam point)

$T_2 = 0°C = 0 + 273 = 273$ K (ice point)

So, $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{273}{373} = \frac{373 - 273}{373} = \frac{100}{373}$

$$\% \text{ of efficiency } = \frac{100}{373} \times 100 = 26.81\%$$

Problem: A Carnot engine whose temperature of the source is 400 K takes 200 calories of heat at this temperature and reject 150 calories of heat to the sink. What is temperature of the sink. Also calculate the efficiency of the engine?

Soln. $Q_1 = 200\ Cal$, $Q_2 = 150$ Cal, $T_1 = 400$ K, $T_2 = ?$

Using $\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \Rightarrow T_2 = \frac{Q_2}{Q_1} \times T_1 = \frac{150}{200} \times 400 = 300\ K$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25$$

% of efficiency $= 0.25 \times 100 = 25\%$.

CAREER ENDEAVOUR

Problem: A Carnot engine is operated between two reservoirs at temperature of 450 K and 350 K. If the engine receives 1000 calories of heat from the source in each cycle. Calculate the amount of heat rejected to the sink in each cycle. Calculate the efficiency of the engine & the work done by the engine in each cycle (1 calorie = 4.2J)

Soln. $T_1 = 450$ K, $T_2 = 350$K, $Q_1 = 1000$ cal, $Q_2 = ?$

Using, $\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \Rightarrow Q_2 = \frac{T_2}{T_1} \times Q_1 = \frac{350}{450} \times 1000 = 777.77\ cal.$

So, $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{350}{450} = \frac{100}{450} = 0.2222$

So, % of efficiency =22.22%

Also, work done in each cycle = $Q_1 - Q_2$

$= (1000 - 777.77)$ cal $= 222.23$ cal

$= 222.23 \times 4.2$ J $= 933.336$ J

Problem: A Carnot engine whose low temperature reservoir is at 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the high temperature reservoir be increased?

Soln. In the Case-I:

$\eta = 50\% = 0.5$, $T_2 = 273 + 7 = 280$ K, $T_1 = ?$

$$So, \quad \eta = 1 - \frac{T_2}{T_1} \Rightarrow 0.5 = 1 - \frac{280}{T_1}$$

$$\Rightarrow \quad \frac{280}{T_1} = 0.5 \quad \Rightarrow \quad T_1 = \frac{280}{0.5} = \frac{2800}{5} = 560\ K$$

In the Case-II:

$\eta = 70\% = 0.7$

$T_2 = 280K$, $T_1 = ?$

$$So, \eta = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow 0.7 = 1 - \frac{280}{T_1} \Rightarrow \frac{280}{T_1} = 0.3 \Rightarrow T_1 = \frac{280}{0.3} = \frac{280}{3} = 933.33\ K$$

So increase in temperature = 933.33 – 560 = 373.33 K

Problem: In a Carnot cycle isothermal expansion of an ideal gas take place at 400 K and the isothermal compression at 300 K during the expansion 500 cal of heat energy are transfered to the gas. Determine

(1) The work performed by the gas during isothermal expansion.

(2) The heat rejected from the gas during an isothermal compression

(3) The work done in isothermal compression of gas?

Soln. (i) The work performed by the gas during the isothermal expansion is equivalent to heat Q_1 absorbed by the gas

Here $Q_1 = 500$ cal $= W/J = Q$

$W = 500 \times 4.18 = 2090$ Joule.

(ii) Let Q_2 be the amount of heat rejected. Then,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_2 = \frac{T_2}{T_1} \times Q_1 = 500 \times \frac{300}{400} = 375\ cal$$

(iii) The work done on the gas during isothermal compression is equivalent to the heat rejected

$$W = Q_2 = 375\ cal = 375 \times 4.18 = 1567.5\ Joule$$

Problem: A reversible engine works between two temperature whose difference is 100°C. If 746 J of heat from the source is taken and 546 J heat is given to the sink by working substance. Calculate the temperature of the source and sink.

Soln. Given $T_1 - T_2 = 100°C$, $Q_1 = 746$ J, $Q_2 = 546$ J

Using $\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow \frac{Q_1}{Q_2} = \frac{746}{546} = \frac{373}{273}$

$$\Rightarrow \quad \frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2} \Rightarrow \frac{200}{546} = \frac{100}{T_2} \Rightarrow T_2 = \frac{546 \times 100}{200} = 273°C$$

Now, $T_1 - T_2 = 100 \Rightarrow T_1 = T_2 + 100 = 273 + 100 = 373°C$.

Problem: An ideal Carnot heat engine takes 1000 cal of heat at 627°C from a source and rejects a part at 27°C to the sink. Find the work done by the engine per cycle. The heat rejected to the sink per cycle and the efficiency of the engine.

Soln. $Q_1 = 1000$ cal, $T_1 = 627°C = 900$ K

$Q_2 = ?$ $\quad T_2 = 27°C = 300$ K

Now, $\dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2} \Rightarrow \dfrac{1000}{x} = \dfrac{900}{300} \Rightarrow x = \dfrac{1000 \times 300}{900} = 333.3\ cal$

So the heat rejected per cycle to the sink = 333.3 cal

Now $W = Q_1 - Q_2 = 1000 - 333.3 = 666.7$ cal $= (666.7 \times 4.18)$ Joules $= 2.786 \times 10^3$ Joules

Now, $\eta = 1 - \dfrac{T_2}{T_1} = 1 - \dfrac{300}{900} = \dfrac{600}{900} = \dfrac{2}{3}$

Problem: The efficiency of a Carnot cycle is 1/6. On reducing the temperature of the sink by 65°C the efficiency increases to 1/3. Find the initial and final temperature between which the cycle is working.

Soln. Using $\eta = 1 - \dfrac{T_2}{T_1} \Rightarrow \dfrac{1}{6} = \dfrac{T_1 - T_2}{T_1} \Rightarrow 6T_1 - 6T_2 = T_1$

or $\quad 5T_1 - 6T_2 = 0$ $\quad \ldots$ (i)

Now, according to question $1 - \dfrac{(T_2 - 65)}{T_1} = \dfrac{1}{3} \Rightarrow \dfrac{T_1 - T_2 + 65}{T_1} = \dfrac{1}{3} \Rightarrow 3T_1 - 3T_2 + 195 = T_1$

Or $\quad 2T_1 - 3T_2 = -195$ $\quad \ldots$ (ii)

Solving equations (i) and (ii),

$5T_1 - 6T_2 = 0 \Rightarrow 5T_1 - 6T_2 = 0 \Rightarrow 2T_1 - 3T_2 = -195$

Solving $T_1 = 390$ K. Also, $5T_1 = 6T_2 \Rightarrow 5 \times 390 = 6T_2$

$\Rightarrow T_2 = \dfrac{5 \times 390}{6} = 325K$

Problem: For a Carnot engine using an ideal gas the adiabatic expansion ratio (ρ) is 5 and value of $\gamma = 1.4$ calculate the efficiency of the engine

Soln. $\eta = 1 - \left(\dfrac{1}{\rho}\right)^{\gamma - 1} = 1 - \left(\dfrac{1}{5}\right)^{1.4-1} = 1 - \left(\dfrac{1}{5}\right)^{0.4} = 0.48$

Problem: Two Carnot engines are operating in series. The I engine absorbs a quantity of heat Q_1 at a temperature T_1 and after doing work W_1 rejects the remaining heat Q_2 at lower temperature T_2. The II engine absorbs the heat Q_2 at temperature T_2 (rejected by I) and after doing work W_2 rejects the remaining heat Q_3 at a still lower temperature T_3. Compute the efficiency of the combination. **[IISc. 2008]**

Soln. $W = (Q_1 - Q_2) + (Q_2 - Q_3) = Q_1 - Q_3$

η (efficiency) $= \dfrac{W}{Q_1} = \dfrac{Q_1 - Q_3}{Q_1} = 1 - \dfrac{Q_3}{Q_1}$

But $\quad \dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}$ and $\dfrac{Q_1}{Q_3} = \dfrac{T_1}{T_3}$

So, $\quad \eta = 1 - \dfrac{T_3}{T_1}$

Adiabatic Expansion Ratio (ρ)

It is defined as the ratio of the initial and final volumes in an adiabatic expansion process.

Since, BC is an adiabatic process, $\rho = \frac{V_3}{V_2}$

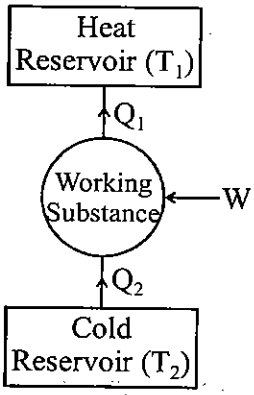
Then, from (7), $\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{1}{\rho}\right)^{\gamma-1}$

$\therefore \quad \eta = 1 - \frac{T_2}{T_1} = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}$

Refrigerator and Heat Pump

A *refrigerator* is the reverse of a heat engine. Here the working substance extracts heat Q_2 from the cold reservoir at temperature T_2, some external work W is done on it and heat Q_1 is released to the hot reservoir at temperature T_1.

The Schematic diagram of a refrigerator is



The efficiency of a refrigerator is measured by the coefficient of performance (K). It is defined as the ratio of the heat extracted from the cold reservoir Q_2 to the work done W, by an external agent.

So we have

$$K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \qquad \ldots (19)$$

$$\Rightarrow \quad \boxed{K = \frac{T_2}{T_1 - T_2}} \qquad \ldots (20) \qquad [\text{From (12)}]$$

The coefficient of performance of a refrigerator, unlike the thermal efficiency of a heat engine, can be much larger than 1 or 100 % but can't be infinite. If its value gets infinity, it means that there is no need of any work to be performed to extract heat from the cold reservoir and to release it into the hot reservoir. A good refrigerator should have high value of K.

A heat pump is the same as refrigerator. What term we use depends on the purpose of the device. If the purpose is to cool a portion of space, the device is said to be a refrigerator. If the idea is to pump heat into a portion of space, the device is called a *heat pump*.

Problem: A heat pump working on the Carnot cycle maintains the inside temperature of a house at 22°C by suppling 450 kJ s^{-1}. If the outside temperature is 0°C, the heat taken, in kJ s^{-1}, from the outside air is approximately.

(a) 487 (b) 470 (c) 467 (d) 417

Soln. The efficiency of Carnot heat engine may be defined as

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

where, Q_1 is heat taken from the source by working substance and Q_2 is the heat given by working substance to sink respectively. Also, T_1 and T_2 are the temperatures of source and sink respectively. Hence, in question

$Q_1 = 450$ kJ/s, $Q_2 = ?$

$T_1 = 22 + 273 = 295$ K,

$T_2 = 273\ K$

Hence, $\frac{450 - Q_2}{450} = \frac{295 - 273}{295}$ or $Q_2 = \frac{273 \times 450}{295} = 416.44$ kJ/s $\cong$ 417 kJ/s

Hence correct option is (d).

Negative Temperature

From efficiency of Carnot engine, $\eta = 1 - \frac{T_2}{T_1}$

If suppose the efficiency gets greater than 1, i.e., $\eta > 1$

$$\Rightarrow 1 - \frac{T_2}{T_1} > 1$$

$$\Rightarrow T_2 < 0 \qquad \text{... (21)}$$

This is not possible as T_2 should always be greater than zero (by definition).

Problem: A Carnot refrigerator taken heat from water at 0 °C and discard it to a room at 27 °C. What is the value of the coefficient of its performance ?

(a) 11.1 (b) 111.0 (c) 1.11 (d) 0.111

Soln. Given : $T_1 = 27\,°C = 300$ K and $T_2 = 0\,°C = 273$ K

The coefficient of performance is

$$K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

$$= \frac{273}{300 - 273} = \frac{273}{27} = 111.0$$

Correct option is (b)

Problem: A Carnot engine working as a refrigerator between 260 K and 300 K receives 500 calories of heat from the reservoir at the lower temperature calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of workdone in each cycle to operate the refrigerator.

Soln. $Q_1 = ?$, $Q_2 = 500$ cal , $T_1 = 260$K, $T_2 = 300$K

For Carnot engine:

$$\frac{Q_1}{T_1}=\frac{Q_2}{T_2}\Rightarrow Q_1=\frac{Q_2}{T_2}\times T_1=\frac{5000\times 260}{300}=576.92cal$$

So, $W=Q_1-Q_2=76.92$ cal $=76.92\times 4{\cdot}2=323.06$ Joule.

Problem: A Carnot's refrigerator takes heat from water at 0°C and discard it to a room at 27°C. 1 kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat are discarded to the room? What is the work done by the refrigerator in this process? What is the co-efficient of performance of the machine? (L_f=80 cal/g)

Soln. $Q_1=?$, $Q_2=mL_f=1000\times 80=80{,}000$ cal

$T_1=300K$, $T_2=273K$

For Carnot engine,

$$\frac{Q_1}{Q_2}=\frac{T_1}{T_2}\Rightarrow Q_1=\frac{T_1}{T_2}\times Q_2=\frac{80000\times 300}{273}=87{,}900\,cal.$$

Work done by the refrigerator is

$$W=(Q_1-Q_2)=4.2(87900-80000)J$$
$$=4.2\times 7900=3.183\times 10^4\ \text{J}$$

$$\text{Co-efficient of performance}=\frac{Q_2}{Q_1-Q_2}=\frac{80{,}000}{87900-80{,}000}=\frac{80{,}000}{7900}=10.13$$

Relation between 'η' and '*K*'

By definition

$$\eta=1-\frac{T_2}{T_1}=\frac{T_1-T_2}{T_1} \qquad \text{... (22)}$$

and $K=\dfrac{T_2}{T_1-T_2}$ ... (23)

Now, $K+1=\dfrac{T_2}{T_1-T_2}+1=\dfrac{T_1}{T_1-T_2}=\dfrac{1}{\eta}$ [From (22)]

$$\Rightarrow \eta=\frac{1}{K+1} \qquad \text{... (24)}$$

$$\Rightarrow \boxed{K=\frac{1}{\eta}-1} \qquad \text{... (25)}$$

Carnot Theorem

1. No engine working between two given temperatures can be more "efficient" than a reversible (Carnot engine) engine, working between the same limits of temperature.
2. All reversible engine (Carnot engine) working between the same limits of temperature have the same efficiency, whatever be the working substance.

Problem: Two identical bodies of constant heat capacities at temperature T_1 and T_2 $(T_1>T_2)$ are used as reservoirs for a heat engine. Assuming that the bodies don't undergo any phase change and remain at constant pressure P. Show that the amount of work obtained is given by

$$W=C_P(T_1+T_2-2T_f)$$

where, T_f is the final temperature of the bodies. Also show that W is maximum when $T_f=\sqrt{T_1T_2}$

Soln. The working substance takes heat from the body at temperature T_1 and after doing work gives the balance heat to the body at temperature T_2. This process continues until T_1 drops to T_f and T_2 rises to T_f

The total heat taken from the hot body

$$Q_1 = C_P\left(T_1 - T_f\right) \quad \text{... (i)}$$

and the heat given to the cold body

$$Q_2 = C_P\left(T_f - T_2\right) \quad \text{... (ii)}$$

The balance (Q_1–Q_2) converts into work, i.e.,

$$W = Q_1 - Q_2 = C_P\left(T_1 - T_f\right) - C_P\left(T_f - T_2\right)$$

$$W = C_P\left(T_1 - T_f - T_f + T_2\right) = C_P\left(T_1 + T_2 - 2T_f\right)$$

The heat Q_1 is taken in at a mean temperature $= \dfrac{T_1 + T_f}{2}$

and the heat Q_2 is given out at a mean temperature $= \dfrac{T_2 + T_f}{2}$

Carnot engine have maximum efficiency so the work done must be maximum

$$\frac{Q_1}{Q_2} = \frac{\dfrac{T_1 + T_f}{2}}{\dfrac{T_2 + T_f}{2}} = \frac{T_1 + T_f}{T_2 + T_f}$$

From equations (i) and (ii),

$$\frac{Q_1}{Q_2} = \frac{T_1 - T_f}{T_f - T_2}$$

$$So \quad \frac{T_1 + T_f}{T_2 + T_f} = \frac{T_1 - T_f}{T_f - T_2}$$

$$\Rightarrow \quad T_f = \sqrt{T_1 T_2}$$

CAREER ENDEAVOUR

PROBLEMS TO BE PLAYED

1. Which of the following is correct?

(a) $\frac{T_1}{H_2}+\frac{T_2}{H_1}=0$ (b) $\frac{H_1}{T_1}=\frac{H_2}{T_2}$ (c) $H_1T_1=H_2T_2$ (d) $H_1T_1+H_2T_2=0$

2. The device which converts heat into mechanical work is–

(a) Motor (b) Generator (c) Heat engine (d) Energy converter

3. A reversible heat engine can have 100% efficiency if the temperature of sink is–

(a) Less than that of source (b) Equal to that of source

(c) 0°C (d) 0 K

4. In a heat engine the maximum heat that can be converted into mechanical work–

(a) Depends upon friction (b) Depends upon working temperatures

(c) Is 100% (d) Depends upon the working

5. The change in entropy is–

(a) Positive in a reversible change (b) Negative in an irreversible change

(c) Positive in an irreversible change (d) Negative in a reversible change

6. If T_1 and T_2 are the temperatures of two reservoirs (where $T_1 > T_2$) and a Carnot engine being operated between them will have the efficiency

(a) $\frac{(T_1-T_2)}{T_2}$ (b) $\frac{(T_1-T_2)}{T_1}$ (c) $\frac{T_1}{(T_1-T_2)}$ (d) $\frac{T_2}{(T_1-T_2)}$

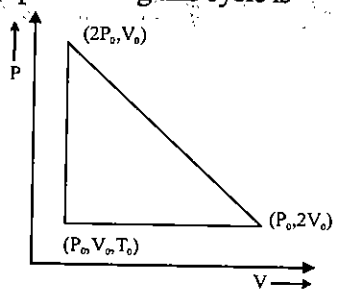
7. The efficiency of a heat engine working between heat reservoirs at temperature 327 °C and 27°C respectively is

(a) 25° (b) 50° (c) 75° (d) 100°

8. In a reversible cycle, the value of the integral $\oint \frac{dQ}{T}$ is–

(a) $\oint \frac{dQ}{T}>0$ (b) $\oint \frac{dQ}{T}<0$ (c) $\oint \frac{dQ}{T}=0$ (d) $\oint \frac{dQ}{T}=$ constant

9. The work of a reversible heat engine performing this cycle is–



(a) $\frac{1}{2}$ (b) $\frac{1}{6}$ (c) $\frac{1}{8}$ (d) $\frac{1}{10}$

10. If an ideal (frictionless) heat enegine absorbs heat at a temperature 100°C and exhausts heat at a temperature 0 °C, its efficiency is 100%. This statements is

(a) True (b) False

(c) Uncertain (d) Needs more information

11. A heat engine works on a Carnot cycle with a heat sink at a temperature of 27°C. The efficiency of the engine is 10%. The approximate temperature of the heat source is
(a) 30 K (b) 270 K (c) 60°C (d) 30 °C

12. An ideal engine absorbs heat at a temperature of 127 °C and exhausts heat at a temperature of 77°C. Its efficiency is approximately
(a) 13% (b) 39% (c) 61% (d) 74%

13. The efficiency of a Carnot engine using an idal gas as the working substance is
(a) $\frac{T_1 - T_2}{T_1}$ (b) $\frac{T_1}{T_1 - T_2}$ (c) $T_1(T_1 - T_2)$ (d) $T_2(T_1 - T_2)$

14. The efficiency of a Carnot's cycle is given by (in terms of compression ratio represented by ρ)
(a) $\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma - 1}$ (b) $\eta = 1 - (\rho)^{\gamma - 1}$ (c) $\eta = 1 - \left(1 - \frac{1}{\rho}\right)^{\frac{1}{\gamma - 1}}$ (d) $\eta = 1 - (\rho)^{\gamma}$

15. The efficiency of a Carnot engine between the source at absolute temperature T_1 and the sink at an absolute tem,perature T_2 is given by
(a) $\frac{1}{T_1} \times T_2 \times 100$ (b) $\left(\frac{T_1}{T_2} - 1\right) \times 100$ (c) $\left(1 - \frac{T_2}{T_1}\right) \times 100$ (d) $\frac{T_2}{T_1} \times 100$

16. In a Carnot engine for a certain difference in temperature between the source T_1 and T_2, the efficiency η
1. can be increased to a larger extent by increasing the source temperature
2. can be increased to a larger extent by decreasing the sink temperature
3. is independent of the working substance in the cycle
4. is same as that of an irreversible engine based on the Carnot cycle with the same T_1 and T_2
(a) only 4 (b) 1 and 3 (c) 2 and 3 (d) only 3

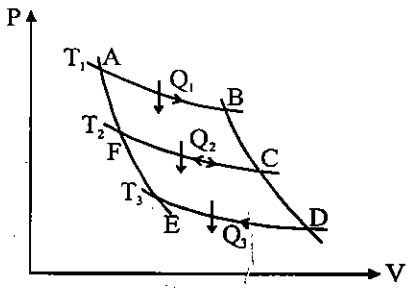
ANSWER KEY

1. (b)	**2. (c)**	**3. (d)**	**4. (b)**	**5. (c)**	**6. (b)**	**7. (b)**
8. (c)	**9. (a)**	**10. (b)**	**11. (a)**	**12. (a)**	**13. (a)**	**14. (b)**
15. (c)	**16. (c)**					

Chapter 4

The Entropy & The Second Law of Thermodynamics

Entropy (S)



[Diagram showing two Carnot ABCF and FCDE]

Let ABCF and FCDE represent two Carnot cycles. Let Q_1 amount of heat entered in the system in the process A to B at temperature T_1 and let Q_2 amount of heat rejected from the system in the process C to D at temperatue T_2.

Then from Carnot's theorem,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \ldots (1)$$

CAREER ENDEAVOUR

Similarly in the cycle if Q_2 be the heat entered in the system at temperature T_2 and Q_3 be the heat liberated out of the system at temperature T_3, then by the Carnot's theorem

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_3} \quad \ldots (2)$$

where the curves AFE and BCD are the adiabatics.

So if Q be the amount of heat absorbed or rejected at a temperature T in going from one adiabatic to the other then,

$$\frac{Q}{T} = \text{Constant} \quad \ldots (3)$$

This constant quantity is called *change in entropy* between the state represented by the two adiabatics. If two adiabatics are very closed then, change in entropy is given by

$$dS = \frac{dQ}{T} \quad \ldots (4)$$

It is a state function. The change in the entropy for a finite change is

$$\int_1^2 dS = \int_1^2 \frac{dQ}{T} \quad \ldots (5)$$

$$\Rightarrow \quad \boxed{S_2 - S_1 = \Delta S = \int_1^2 \frac{dQ}{T}} \qquad \ldots (6)$$

Problem: The entropy function of system is given by S(E) = a E (E_0 – E) where a and E_0 are positive constants. The temperature of the system is

(a) negative for some energies (b) increases monotonically with energy
(c) decreases monotonically with energy (d) zero

Soln. $\frac{1}{T} = \frac{dS}{dE} \Rightarrow \frac{1}{T} = a E_0 - 2aE \Rightarrow T = \frac{1}{(a E_0 - 2aE)}$.

This means that T is continuous and will be positive for $E > 2E_0$ and negative for $E < 2E_0$.

Hence correct option is (a).

Problem: Experimental measurements of heat capacity per mole of aluminium at low temperatures. Show that the data can be fitted to the formula, $C_v = aT + bT^3$, where $a = 0.00135\, JK^{-2}\ \text{mol}^{-1}$, $b = 2.48 \times 10^{-5} J\, K^{-4}\ \text{mol}^{-1}$ and T is the temperature in Kelvin. The entropy of a mole of aluminium at such temperature is given by

(a) $aT + \frac{bT^3}{3} + C$, C is a constant (b) $\frac{aT}{2} + \frac{b}{4}T^3 + C$, C is a constant

(c) $aT + \frac{6}{3}T^3$ (d) $\frac{aT}{2} + \frac{b}{4}T^3$

Soln. Given : $C_v = aT + bT^3$

The entropy of a mole is

$$\Delta S = \int \frac{dQ}{T} = \int \frac{C_v\, dT}{T} = \int \left(a + bT^2\right) dT$$

$= aT + \frac{bT^3}{3} + C$, where C is a constant.

CAREER ENDEAVOUR

Correct option is (a)

Problem: In a certain process, the temperature (T) and entropy (S) are related by $T \propto S^n$, where n is a number. What is the heat capacity in terms of the entropy of the process?

(a) $\frac{S^2}{k_B n^2}$ (b) $\frac{S}{n}$ (c) $n k_B e^{S/k_B}$ (d) $n\sqrt{S k_B}$

Soln. Given : $T = K S^n$, K is a constant

Since $dS = \frac{dQ}{T} = \frac{CdT}{T}$

$$\Rightarrow \quad C = T\frac{dS}{dT} = \frac{T}{dT/dS}$$

$$\Rightarrow \quad C = \frac{KS^n}{nKS^{n-1}} = \frac{S}{n}$$

Correct option is (b)

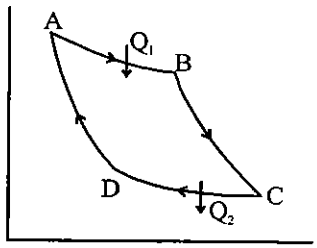
Problem: Which of the following integrals depends only on the initial and final states of a thermodynamic system (i.e., independent of the path of transformation)?

(a) $\int PdV$ (b) $\int dQ$ (c) $\int \frac{dQ}{T}$ (d) $\int T^2 dS$ **[JNU : 2009]**

Ans. (c) Since, entropy is a state function and $\Delta S = \int \frac{dQ}{T}$

Change in Entropy in Some Processes

(1) Reversible Process: Consider a reversible process (Carnot cycle) ABCD. Then, change in entropy in process A to B



$$\Delta S_1 = \frac{Q_1}{T_1}$$

In process B to C,

$\Delta S_2 = 0$ (BC is an adiabatic process)

In process C to D,

$$\Delta S_3 = -\frac{Q_2}{T}$$

In process D to A,

$\Delta S_4 = 0$ (DA is an adiabatic process)

So total change in the entropy is

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \quad \ldots (7)$$

By Carnot theorem,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Therefore, equation (7), $\Rightarrow \Delta S = 0$

CAREER ENDEAVOUR

"So there is no change in the entropy in a reversible process."

Now from equation (5),

$$\boxed{\oint dS = \oint \frac{dQ}{T} = 0} \quad \ldots (8)$$

Problem: A Carnot cycle operates as a heat engine between two bodies of equal heat capacity until their temperatures become equal. If the initial temperatures of the bodies are T_1 and T_2, respectively, and $T_1 > T_2$ then their common final temperature is

(a) T_1^2 / T_2 (b) T_2^2 / T_1 (c) $\sqrt{T_1 T_2}$ (d) $\frac{1}{2}(T_1 + T_2)$

Soln. Carnot cycle is reversible cycle so the entropy change must be zero.

$\Delta S = 0$

Let the equilibrium temperature be T then

$\Delta S = C\int_{T_1}^{T} \frac{dT}{T} + C\int_{T_2}^{T} \frac{dT}{T} = 0$; where C is the heat capacity

$$\Rightarrow \ln\left(\frac{T}{T_1}\right)+\ln\left(\frac{T}{T_2}\right)=0$$

$$\Rightarrow \ln\left(\frac{T^2}{T_1T_2}\right)=0 \Rightarrow T^2=T_1T_2 \Rightarrow T=\sqrt{T_1T_2}$$

Correct answer is (c)

Problem: Consider two identical blocks of constant specific heat capacity, one of which is at temperature T_1 and the other at T_2. A reversible engine transfers heat from the hotter block to the colder until they reach the same temperature which is

(a) $\sqrt{T_1T_2}$ (b) $\frac{T_1+T_2}{2}$ (c) $\frac{T_1T_2}{T_1+T_2}$ (d) T_2

Soln. Let the final temperature be T. Then,

$$\Delta S=(\Delta S)_1+(\Delta S)_2$$

$$=C\int_{T_1}^{T}\frac{dT}{T}+C\int_{T_2}^{T}\frac{dT}{T}=C\ln\left(\frac{T^2}{T_1T_2}\right), \text{ where } C \text{ is the specific heat capacity}$$

For reversible process $\Delta S=0$

$$\Rightarrow \ln\left(\frac{T^2}{T_1T_2}\right)=0 \Rightarrow T=\sqrt{T_1T_2}$$

Correct option is (a)

(2) Irreversible Process:

The efficiency in any heat engine (may be reversible or irreversible) is

$$\eta=1-\frac{Q_2}{Q_1} \qquad \text{... (9)}$$

CAREER ENDEAVOUR

and in Carnot heat engine (reversible engine) is

$$\eta'=1-\frac{T_2}{T_1} \qquad \text{... (10)}$$

The Carnot theorem says that the efficiency of a reversible Carnot engine is maximum. So

$$1-\frac{T_2}{T_1}\geq 1-\frac{Q_2}{Q_1} \Rightarrow \frac{Q_2}{Q_1}\geq\frac{T_2}{T_1} \Rightarrow \frac{Q_2}{T_2}-\frac{Q_1}{T_1}\geq 0$$

$$\Rightarrow \quad \boxed{\Delta S\geq 0} \qquad \text{... (11)}$$

The equality holds here for reversible engine.

Equation (11) says that the entropy always increases in an irreverssible process.

(3) Reversible Adiabatic Process:

In any adiabatic process, $dQ=0$ and hence $dS=0$.

It means that there is no change in the entropy in a reversible adiabatic process. Such an adiabatic process is called "isentropic".

(4) Reversible Isothermal Process:

The change in entropy is

$$\Delta S = \int \frac{dQ}{T}$$

Since T remains constant in an isothermal process, so we have

$$\Delta S = \frac{1}{T}\int_{Q_2}^{Q_1} dQ = \frac{1}{T}(Q_1 - Q_2)$$

where Q_1 and Q_2 are the amount of heat absorbed and rejected respectively. Henceforth, $Q_1 - Q_2$ is the amount of work done (ΔW).

So, $\Delta S = \frac{\Delta W}{T}$

where $(\Delta W)_{\text{isothermal}} = nRT\ \ell n\left(\frac{V_2}{V_1}\right)$

$$\therefore \quad \boxed{\Delta S = nR\ \ell n\left(\frac{V_2}{V_1}\right)} \qquad \ldots (12)$$

where V_1 and V_2 are the initial and final volumes of the gas in the system.

Problem: An ideal gas undergoes an isothermal expansion (at a constant temperature T) from an initial volume V_1 to a final volume V_2. The change in the entropy per mole is

(a) $R\left(\frac{V_1}{V_2}\right)$ (b) $R\ln|V_1 - V_2|$ (c) $R\ln\left(\frac{V_1}{V_2}\right)$ (d) $R\ln\left(\frac{V_2}{V_1}\right)$

Soln. For isothermal expansion, $Q = W = nRT\ln\left(\frac{V_2}{V_1}\right)$

$$\therefore (\Delta S)_{\text{isothermal}} = \int \frac{dQ}{T} = \frac{1}{T}\int dQ = nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow (\Delta S)_{\text{isothermal}} = R\ln\left(\frac{V_2}{V_1}\right) \qquad [\because \text{For 1 mole}]$$

Correct option is (d)

Problem: A sample of ideal gas with initial pressure P and volume V is taken through an isothermal expansion process during which the change in entropy is found to be ΔS. The universal gas constant is R. Then the work done by the gas is given by

(a) $(PV\Delta S)/(nR)$ (b) $nR\Delta S$ (c) PV (d) $(P\Delta S)/(nRV)$

Soln. By ideal gas equation, $PV = nRT$ ...(i)

and $\Delta S = \frac{\Delta Q}{T}$ ...(ii)

Multiplying equations (i) and (ii),

$$PV\Delta S = nR\Delta Q$$

$$\Rightarrow \quad \Delta Q = \frac{PV\Delta S}{nR}$$

$\because$ For isothermal expansion, $\Delta U = 0$

$$\Rightarrow \quad W = \Delta Q = \frac{PV\Delta S}{nR}$$

Hence correct option is (a).

(5) Reversible Isobaric Process:

The change in the entropy is

$$\Delta S = \int \frac{dQ}{T} \quad \text{where} \quad dQ = C_P dT$$

$$\therefore \quad \Delta S = \int_{T_1}^{T_2} C_P \frac{dT}{T}$$

If C_P remains constant in the range T_1 and T_2, then

$$\boxed{\Delta S = C_P \, \ell n\left(\frac{T_2}{T_1}\right)} \qquad \ldots (13)$$

(6) Reversible Isochoric Process:

The entropy change is

$$\Delta S = \int \frac{dQ}{T}$$

where $dQ = C_V \, dT$

$$\therefore \quad \Delta S = \int_{T_1}^{T_2} C_V \frac{dT}{T}$$

CAREER ENDEAVOUR

If there is no change in the value of C_V for the range T_1 and T_2, then

$$\boxed{\Delta S = C_V \, \ell n\left(\frac{T_2}{T_1}\right)} \qquad \ldots (14)$$

(7) Irreversible Process (an another approach)

The another way of concluding the entropy always increases in a irrevsible process is as follows:

Let our system having heat capacity C and at temperature T_1 is in contact with a reservoir at temperature $T_2 (T_2 > T_1)$. So some amount of heat flows from reservoir to the system. If there is a finite temperature difference between initial and final state of the system and if the process is isochoric then, the change in the system's entropy is

$$(\Delta S)_{sys} = \int \frac{dQ}{T} = \int_{T_1}^{T_2} C \frac{dT}{T} = C \, \ell n\left(\frac{T_2}{T_1}\right) \qquad \ldots (15)$$

Since $T_2 > T_1$, $(\Delta S)_{sys.} > 0$ $\qquad \ldots (16)$

Also, heat flows in to the system is $Q = C(T_2 - T_1)$

Since the heat capacity of the reservoir is so large, there is no change in the temperature if heat flows in or out of it and since heat flows out of the reservoir, we have

$$(\Delta S)_{\text{Res.}} = \int \frac{dQ}{T_2} = \frac{1}{T_2}\int dQ = -\frac{Q}{T_2} = -\frac{C_V(T_2 - T_1)}{T_2} = -C_V\left(1 - \frac{T_1}{T_2}\right) \quad \ldots (17)$$

Since $T_1 < T_2 \Rightarrow \frac{T_1}{T_2} < 1$, So $(\Delta S)_{res} < 0$.

So the entropy of the reservoir decreases.

The total change in entropy of the composite system, body plus reservoir, is

$$\Delta S = (\Delta S)_{sys.} + (\Delta S)_{res.} = C_V\left[\ell n\left(\frac{T_2}{T_1}\right) - \frac{T_2 - T_1}{T_2}\right]$$

$$= -C_V\left[\ell n\left(\frac{T_1}{T_2}\right) - \frac{T_1}{T_2} + 1\right] \quad \ldots (18)$$

Since $\frac{T_1}{T_2} < 1$, $\ell n\left(\frac{T_1}{T_2}\right) - \frac{T_1}{T_2} + 1 < 0$,

$\Rightarrow \quad \Delta S > 0$

which means the entropy of the composite system always increases in the irreversible process.

Problem: A Carnot cycle operates on a working substance between two reservoirs at temperature T_1 and T_2, where $T_1 > T_2$. During each cycle an amount of heat Q_1 is extracted from the reservoir at T_1 and an amount Q_2 is delivered to the reservoir at T_2. Which of the following statements is incorrect ?

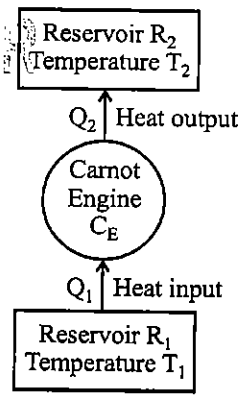
(a) Work done in one cycle is $Q_1 - Q_2$

(b) $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

(c) Entropy of the reservoir decreases

(d) Entropy of the universe (consisting of the working substance and the two reservoirs) increases

Soln. The given Carnot engine is shown schematically in the figure aside.



In ideal case (no energy dissipation)

Work done = Heat input – Heat output

$= Q_1 - Q_2$ ...(i)

($\because$ given $T_1 > T_2 \Rightarrow Q_1 > Q_2$)

Now efficiency of a Carnot cycle $\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$

$$\Rightarrow 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \Rightarrow \boxed{\frac{Q_2}{T_2} = \frac{Q_1}{T_1}} \quad \ldots (ii)$$

Now, $\Delta S = \frac{dQ}{T}$ (definition of entropy)

Since heat is taken away from R_1,

$\Rightarrow \Delta S_{R_1} = -\dfrac{Q_1}{T_1} \Rightarrow$ change in entropy for R_1 is negative

$\Rightarrow$ Entropy of the hotter reservoir decreases ...(iii)

Finally $\Delta S_{universe} = \Delta S_{R_1} + \Delta S_{R_2} + \Delta S_{C_E} = -\dfrac{Q_1}{T_1} + \left(\dfrac{Q_1}{T_1} - \dfrac{Q_2}{T_2}\right) + \dfrac{Q_2}{T_2}$

$\Rightarrow \boxed{\Delta S_{universe} = 0} \Rightarrow (d)$ is incorrect.

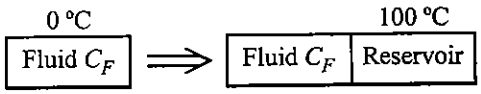
Hence, from (i), (ii) and (iii) we find (a), (b) and (c) are correct. Therefore one has to choose option (d) which is incorrect.

Hence, the correct option is (d).

Problem: A certain amount of fluid with heat capacity C_F Joules/°C is initially at a temperature 0°C. It is then brought into contact with a heat bath at a temperature of 100°C, and the system is allowed to come into equilibrium. In this process, the entropy (in Joules/°C) of the universe changes by

(a) $100\ C_F$ (b) 0 (c) $0.055\ C_F$ (d) $0.044\ C_F$

Soln.



$$(\Delta S)_{\text{universe}} = (\Delta S)_{\text{fluid}} + (\Delta S)_{\text{reservoir}}$$

$$= \int \frac{dQ}{T} + \int \frac{dQ}{T}$$

$$= C_F \int_{T_1}^{T_2} \frac{dT}{T} + \frac{1}{T_2}\int dQ = C_F \int_{T_1}^{T_2} \frac{dT}{T} - \frac{C_F(T_2 - T_1)}{T_2}$$

$$= C_F \ln\left(\frac{T_2}{T_1}\right) - C_F\left(\frac{T_2 - T_1}{T_2}\right)$$

CAREER ENDEAVOUR

where $T_1 = 0\,°\text{C} = 273\ \text{K},\ T_2 = 100\,°\text{C} = 373\ \text{K}$

Therefore, $\Delta S = C_F\left[\ln\left(\dfrac{373}{273}\right) - \dfrac{100}{373}\right] = 0.044\ C_F$

Correct option is (d)

Change in Entropy in Conversion Process System

(1) When a liquid is heated from T_1 to $T_2 (T_2 > T_1)$.

Let a liquid of mass 'm' and specific heat C is heat from T_1 to T_2. If dQ is the amount of heat taken to rise its temperature by dT, then

$$dQ = mC\,dT \qquad \ldots (19)$$

The corresponding change in entropy is

$$dS = \frac{dQ}{T} = \frac{mC\,dT}{T} \qquad \ldots (20)$$

The total entropy change is

$$(\Delta S)_{liq} = \int_{T_1}^{T_2} mC\frac{dT}{T} = mC\,\ell n\left(\frac{T_2}{T_1}\right) \quad \ldots (21)$$

Since, $T_2 > T_1$, $(\Delta S)_{liq} > 0$. It means that the entropy increases if a liquid is heated. Similarly, if $T_2 < T, (\Delta S)_{liq.} < 0$. So the entropy decreases if a liquid is cooled down.

(2) Change in entropy when change of state takes place.

If a substance of mass 'm' and latent heat L is heated to convert into another state, the amount of heat required is

$$Q = mL$$

So, the change in entropy is

$$\Delta S = \int \frac{dQ}{T} = \frac{1}{T}\int dQ$$

where temperature remains constant during change of state.

$$\Rightarrow \quad \Delta S = \frac{mL}{T} \quad \ldots (22)$$

(3) If ice (0°C) melts into water then changes to steam (100°C).

The total change in the entropy is

$$\Delta S_1 = (\Delta S)_{\underset{(0°C)}{ice} \to \underset{(0°C)}{water}} = \frac{mL_f}{T_1} \quad \left[\because\ T_1 = 273\,K \text{ and } L_f \text{ is latent heat of fusion}\right]$$

$$(\Delta S)_2 = (\Delta S)_{\underset{(0°C)}{water} \to \underset{(100°C)}{water}} = mC\,\ell n\left(\frac{T_2}{T_1}\right) \left[\because\ T_2 = 373\,K \text{ and C is specific heat}\right]$$

$$(\Delta S)_3 = (\Delta S)_{\underset{(100°C)}{water} \to \underset{(100°C)}{steam}} = \frac{mL_v}{T_2} \left[\because L_v \text{ is latent heat of vapourisation}\right]$$

$$\therefore \quad (\Delta S)_{Total} = \frac{mL}{T_1} + mC\,\ell n\left(\frac{T_2}{T_1}\right) + \frac{mL}{T_2} \quad \ldots (23)$$

Problem: One kilogram of ice melts at 0°C into water at the same temperature. The change in entropy (cal/K) is $\left(L_f = 3.35 \times 10^5\, J\, kg^{-1}\right)$

(a) ∞ (b) 0 (c) 0.293 (d) 293

Soln. Given : $m = 1$ kg, $L_f = 3.35 \times 10^5$ J/kg^{-1}

$$\Delta S = \frac{Q}{T} = \frac{mL}{T} = \frac{1 \times 3.35 \times 10^5}{273}\ \text{J}$$

$$= \frac{3.35 \times 10^5}{273 \times 4.2} cal \quad \left[\because\ 1 \text{ cal} = 4.2 \text{ J}\right]$$

$$= 292.168 \text{ cal/K} \simeq 293 \text{ cal/K}$$

Correct option is (d)

(4) If a body of mass m_1, specific heat C_1 and temperature T_1 is thermally connected with another body of mass m_2, specific heat C_2 and temperature T_2.

Let $T_1 > T_2$ and T be the equilibrium temperature. Then, according to the principle of calorimetry,

$$m_1 C_1 (T_1 - T) = m_2 C_2 (T - T_2)$$

$$\Rightarrow \quad T = \frac{m_1 C_1 T_1 + m_2 C_2 T_2}{m_1 C_1 + m_2 C_2}$$

The change in the entropy is

$$\Delta S = \Delta S_1 + \Delta S_2 = m_1 C_1 \int_{T_1}^{T} \frac{dT}{T} + m_2 C_2 \int_{T_2}^{T} \frac{dT}{T}$$

$$= m_1 C_1 \, \ell n\left(\frac{T}{T_1}\right) + m_2 C_2 \, \ell n\left(\frac{T}{T_2}\right) = \ell n\left[\left(\frac{T}{T_1}\right)^{m_1 C_1}\left(\frac{T}{T_2}\right)^{m_2 C_2}\right] > 0$$

Change in Entropy in Terms of Different Parameters

(1) Change in entropy of a 'perfect gas' in terms of its pressure, volume and specific heat

Let us consider one mole of perfect gas at pressure P, volume V and temperature T. When an infinitesimal amount of heat dQ is added to it, the increase in entropy is

$$dS = \frac{dQ}{T}$$

From I law, $dQ = dU + dW$

But $dU = C_V dT$ and $dW = PdV = RT\frac{dV}{V}$

So, $$dQ = C_V dT + RT\frac{dV}{V}$$

Now, $$dS = \frac{dQ}{T} = C_V \frac{dT}{T} + R\frac{dV}{V}$$

The total entropy is

$$S = \int \frac{dQ}{T} = C_V \int \frac{dT}{T} + R\int \frac{dV}{V} \qquad \ldots (i)$$

From ideal gas equation, $PV = RT$, we have

$$dT = \frac{PdV + VdP}{R}$$

and $R = C_P - C_V$

$$\therefore \; S = C_V \int \frac{PdV + VdP}{RT} + R\int \frac{dV}{V}$$

$$= C_V \int \frac{PdV + VdP}{PV} + (C_P - C_V)\int \frac{dV}{V}$$

$$= C_V \int \frac{dV}{V} + C_V \int \frac{dP}{P} + C_P \int \frac{dV}{V} - C_V \int \frac{dV}{V}$$

$$= C_V \int \frac{dP}{P} + C_P \int \frac{dV}{V}$$

$$\boxed{S = C_V \log P + C_P \log V + \text{constant}}$$

If a gas passes from an initial state P_i, V_i, T_i to P_f, V_f, T_f then the change in entropy of the gas is

$$\boxed{\Delta S = C_V \log \frac{P_f}{P_i} + C_P \log \frac{V_f}{V_i}}$$

(2) Change in entropy of a perfect gas in terms of its temperature, pressure and specific heat at constant pressure

$$dQ = dU + dW = C_V dT + PdV = C_V dT + RT\frac{dV}{V} = TdS$$

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V}$$

$$\Delta S = \int_i^f dS = \int_i^f \frac{C_V dT}{T} + R\int_i^f \frac{dV}{V} = C_V \ell n \frac{T_f}{T_i} + R\,\ell n \frac{V_f}{V_i}$$

Also, for perfect gas, we have

$$\frac{PV}{T} = \text{constant} \Rightarrow \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \Rightarrow \frac{V_f}{V_i} = \frac{P_i T_f}{P_f T_i}$$

$$\Delta S = C_V\, \ell n \frac{T_f}{T_i} + R\,\ell n \frac{V_f}{V_i} = C_V\, \ell n \frac{T_f}{T_i} + R\,\ell n \frac{P_i}{P_f} + R\,\ell n \frac{T_f}{T_i}$$

$$= C_V\, \ell n \frac{T_f}{T_i} - R\,\ell n \frac{P_f}{P_i} + R\,\ell n \frac{T_f}{T_i}$$

$$= (C_P - R)\,\ell n \frac{T_f}{T_i} - R\,\ell n \frac{P_f}{P_i} + R\,\ell n \frac{T_f}{T_i} \quad (\because C_P - C_V = R)$$

$$= C_P\, \ell n \frac{T_f}{T_i} - R\,\ell n \frac{P_f}{P_i}$$

(3) Change in entropy of a vander Waals' gas as its state changes from V_i, T_i to V_f, T_f:

Equation of state for one mole of vander Waal's gas is

$\left(P + \frac{a}{V^2}\right)(V - b) = RT$ where a, b are vander Waals' constant

$dS = \frac{dQ}{T}$ (Second law of thermodynamics)

$dQ = dU + dW$ (First law of thermodynamics)

where, $dU = C_V dT$ and $dW = \left(P + \frac{a}{V^2}\right)dV = \frac{RT}{V-b}dV \quad \left\{\because P_{eff} = P + \frac{a}{V^2}\right\}$

$$dS = \frac{dQ}{T} = \frac{dU + dW}{T} = \frac{C_V dT + \frac{RT}{(V-b)} dV}{T}$$

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V-b}$$

The change in entropy when the gas passes from the state V_i, T_i to V_f, T_f is:

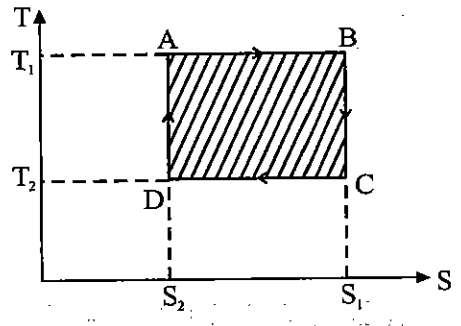
$$\Delta S = S_f - S_i = \int_i^f dS = C_V \int_i^f \frac{dT}{T} + R \int_i^f \frac{dV}{V-b}$$

$$= C_V \ell n \frac{T_f}{T_i} + R \ell n \frac{V_f - b}{V_i - b}$$

$$\boxed{\Delta S = C_V \ell n \frac{T_f}{T_i} + R \ell n \frac{V_f - b}{V_i - b}}$$

Temperature - Entropy Diagram

The Carnot cycle is T-S diagram is represented as:



Since adiabatic process occurs at constant entropy, BC and DA are adiabatics. On the other hand, AB and CD are isothermals.

The area under the curve AB representing any reversible process in a T-S diagram is

$$\int_A^B T\, dS = \int_A^B dQ = Q_{A \to B}$$

So the area under such a curve represents the heat flow in the same way that the area under a curve in a P-V diagram represents work. The area enclosed by the graph of a reversible cyclic process corresponds to the net heat flow into a system in the process.

Efficiency

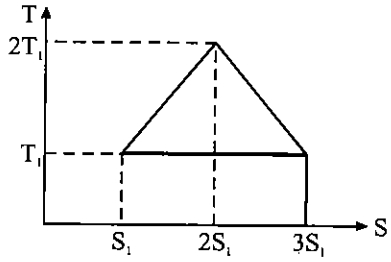
Heat entered into the system $= T_1 (S_1 - S_2)$

Heat goes out of the system $= T_2 (S_1 - S_2)$

The heat converted into work $= (T_1 - T_2)(S_1 - S_2)$

So the efficiency is $\eta = \frac{(T_1 - T_2)(S_1 - S_2)}{T_1 (S_1 - S_2)} \Rightarrow \boxed{\eta = 1 - \frac{T_2}{T_1}}$

Problem: A reversible engine cycle is shown in the following T-S diagram. The efficiency of the engine is-



(a) $\frac{1}{3}$ (b) $\frac{1}{2}$ (c) $\frac{1}{5}$ (d) $\frac{1}{4}$

Soln. The net flow of heat is the area of T-S diagram

i.e., $Q_1 - Q_2 = W = \frac{1}{2} \times (3S_1 - S_1) \times (2T_1 - T_1) = S_1 T_1$

The heat goes out at low temperature T_1. So heat goes out is

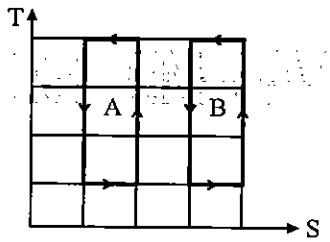
$Q_2 = (3S_1 - S_1) \times T_1 = 2 S_1 T_1$

Therefore, $Q_1 = Q_2 + S_1 T_1 = 3 S_1 T_1$

So, the efficiency is $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{2 S_1 T_1}{3 S_1 T_1} = \frac{1}{3}$

Correct option is (a)

Problem: The entropy temperature diagram of two Carnot engines, A and B are shown in the figure. The efficiencies of the engine are η_A and η_B, respectively. Which one of the following equalities is correct?



(a) $\eta_A = \frac{\eta_B}{2}$ (b) $\eta_A = \eta_B$ (c) $\eta_A = 3\eta_B$ (d) $\eta_A = 2\eta_B$

Soln. The efficiency for a Carnot engine is $\eta = 1 - \frac{T_2}{T_1}$. It means the efficiency depends only on the temperature of the source (T_1) and the temperature of the sink(T_2). Now for engine A and B, T_1 and T_2 are same.

So, $\eta_A = \eta_B$

Correct option is (b)

The Second Law of Thermodynamics

"It states that every process taking place in an isolated system, the entropy of the system either increases (irreversible process) or remains constant (reversible process)."

$$\text{i.e. } (dS \geq 0)$$

- Condition for equilibrium: The necessary condition for the equation of an isolated system is that its entropy shall be a maximum.
- **Clausius Statement:** No process is possible whose sole result is a flow out of one system at a given temperature and a heat flow of the same magnitude into a second system at a higher temperature. It means we must need some work to perform on the system to make the heat to flow from colder region to hotter region.

- **Kelvin-Planck Statement:** No process is possible whose sole result is heat flow Q out of a reservoir at a single temperature out the performance of work W equal in magnitude Q. It means that some heat must extract out of the system to the reservoir. It means that the efficiency of heat engine can never be greater than unity.

The Third Law of Thermodynamics

It states that the entropy of all the perfect crystalline solids is zero at absolute to zero temperature. It is also referred as *Nernst law*. It provides the basis for the calculation of absolute entropies of the substances. Mathematically,

$$\lim_{T \to 0} S = 0$$

PROBLEMS TO BE PLAYED

1. The combined form of first and second law of thermodynamics is given by–
(P = Pressure, V= Volume, T = Temperature, U = Internal energy, S = Entropy, Q = Quantity of heat)
(a) $TdS = dU + PdV$ (b) $dQ = TdS$
(c) $dU = TdS + dQ$ (d) $TdS = dU - PdV$

2. A given amount of heat cannot be completely converted into work. However it is possible to convert a given amount of work completely into heat. This statement results from the
(a) Zeroth law of thermodynamics (b) First law of thermodynamics
(c) Second law of thermodynamics (d) Third law of thermodynamics

3. One kilogram of ice melts at 0°C into water at the same temperature. The change in entropy is (in cal/K)–
(a) ∞ (b) 0
(c) 0.293 (d) 293

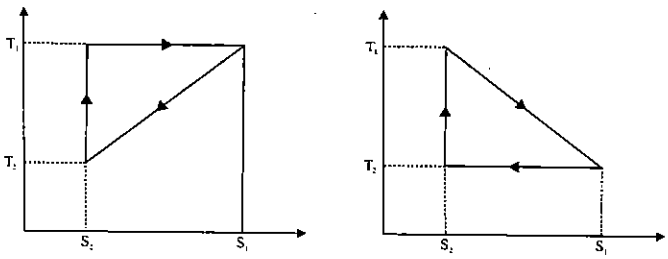
4. "A physical or chemical change takes place in such a way that the entropy either decreases or remains unchanged." This statement is
(a) True universally (b) True only for open system
(c) True only for closed system (d) Not true

5. Change in entropy depends–
(a) Only on the transfer of heat (b) Only on change of temperature
(c) On transfer of mass (d) On the thermodynamic state

6. Two ends of a rod are kept at 127° C and 227°C. When 2000 cal of heat flows in this rod, trhen the change in entropy is
(a) 1.0 cal/K (b) 20 cal/K (c) 6.9 cal/K (d) 0.7 cal/K

7. On a (T – f) diagram, *i.e.*, temperature (T) and entropy (f), the isothermals are
(a) Parallel to f axis
(b) Parallel to T-axis
(c) Some parallel to T and some parallel to f axis
(d) None of the these

8. The T – S diagram of two cycle for the operation of an engine are shown in figures below:



The numerical values of the parameters T_1, T_2, S_1 and S_2 in the two figures are the same which cycle has greater efficiency?
(a) First (b) Second
(c) Both have equal efficiency (d) None

9. For any process, the second law of thermodynamics requires that the change of entropy of the universe be
(a) positive only (b) positive or zero (c) zero only (d) negative or zero

10. On a (T-S) diagram, adiabatics are lines
(a) having any indication
(b) parallel to the T-axis
(c) parallel to the S-axis
(d) some parallel to the S-axis and some parallel to the T-axis.

11. Which of the following is a property of entropy?
(a) Entropy increase during an irreversible operation
(b) Net change in entropy in a reversible cycle is zero
(c) Change in entropy during an adiabatic operation is zero
(d) All of the above

12. At 0 K fluids are assumed to have
(a) Minimum entropy (b) Maximum entropy
(c) Zero entropy (d) Fixed value of entropy

13. The difference in entropy between a state of volume V_i and a state of volume V_f (temperature and no. of molecules remaining constant) is equal to
(a) $nR\log\frac{V_f}{V_i}$ (b) $nR\log\frac{V_i}{V_f}$ (c) $nR^2\log\frac{V_f}{V_i}$ (d) $nR^2\log\frac{V_i}{V_f}$

14. An engine absorbs heat at a temperature of 1000 K and rejects heat at 600 K. If the engine operates at maximum possible efficiency, the amount of work performed by the engine for 200 J heat input is
(a) 1600 J (b) 1200 J (c) 800 J (d) 400 J

15. A mass m of water at temperature T_1 K is isobarically and adiabatically mixed with an equal mass of water at T_2 K. The entropy change of the universe is–
(a) $2mC_P\frac{T_1}{T_2}$ (b) $2mC_P In\frac{T_1+T_2}{2\sqrt{T_1T_2}}$ (c) $2mC_P In\frac{(T_1+T_2)}{2}$ (d) None of these

16. In a reversible process the change in entropy of the system–
(a) Increase (b) Decreases (c) Zero (d) Remains constant

17. In an irreversible adiabatic change in entropy–
(a) Increases (b) Decreases (c) Remains constant (d) Zero

18. Entropy remains constant in–
(a) Isothermal process (b) Adiabatic process (c) Cyclic process (d) Isobaric process

19. The are of the Carnot cycle on a T–S diagram represents–
(a) Heat absorbed from the source (b) Work done in a cycle
(b) Heat rejected to the sink (d) Efficiency of the engine

20. The value of entropy at absolute zero of temperature would be
(a) zero for all the materials
(b) finite for all the materials
(c) zero for some materials and non-zero for others
(d) unpredictable for any materials

ANSWER KEY

1. (a)	**2. (c)**	**3. (d)**	**4. (d)**	**5. (d)**	**6. (b)**	**7. (a)**
8. (b)	**9. (a)**	**10. (c)**	**11. (d)**	**12. (c)**	**13. (a)**	**14. (c)**
15. (b)	**16. (c)**	**17. (a)**	**18. (c)**	**19. (b)**	**20. (a)**	

Chapter 5

Thermodynamic Potentials & Maxwell Relations

Thermodynamic Potentials

Thermodynamic potentials are scalar quantities used to represent the themodynamic state of a system. They measure the energy of a system in terms of different variables because often we can only measure certain properties of the systems. For example, we might know the pressure and temperature of system but not the volume or the entropy. Thermodynamic potential allow us to measurse more state variables of the system. There are four thermodynamics potentials. They are :

1. Internal energy (U)
2. Enthalpy (H)
3. Helmholtz function (F)
4. Gibbs function (G)

1. Internal energy (U) : It is the sum total of internal molecular kinetic and potential energy of the system. It is a state function. By first law of thermodynamics the internal energy is given by

$$dU = dQ - dW \quad \ldots (1)$$

where $dW = PdV$ and $dQ = TdS$

So, we have $dU = TdS - PdV$ ... (2)

Now keeping volume (V) constant in Eq. (2), we get

CAREER ENDEAVOUR

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \ldots (3)$$

and now keeping entropy (S) constant in Eq. (2), we have

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \quad \ldots (4)$$

Now, from Eq. (3), $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial^2 U}{\partial V\,\partial S}\right)_S$ ... (5)

and from Eq. (4), $-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial^2 U}{\partial S\,\partial V}\right)_V$ ... (6)

Exploiting $\frac{\partial^2 U}{\partial V\,\partial S} = \frac{\partial^2 U}{\partial S\,\partial V}$, we get $\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$ ... (7)

2. **Enthalpy (H) :** Changes of phase are always associated with changes in volume, so that work is always done on or by a system in a phase change. If the change takes place at constant temperature, the pressure is constant also and the work done by the system is therefore,

$$W = P(V_2 - V_1) \qquad \ldots (8)$$

where V_1 and V_2 are the initial and final volumes. Then from the first law, the change in internal energy is

$$U_2 - U_1 = L - P(V_2 - V_1) \qquad \ldots (9)$$

where L is the heat supplied by or extracted out the system and known as latent heat or heat of transformation. This equation gives,

$$L = (U_2 + PV_2) - (U_1 + PV_1) \qquad \ldots (10)$$

The sum $(U + PV)$ is defined as the enthalpy (H)

i.e., $H = U + PV$ ... (11)

Therefore, $L = H_2 - H_1$

The heat of transformation in any change of phase is equal to the difference between the enthalpies of the system in the two phase.

Now, using Eq. (11), we have

$$dH = dU + PdV + VdP$$

$$= TdS - PdV + PdV + VdP \qquad \text{[Since using (2)]}$$

Equation (12) gives at constant pressure, $dH = TdS$. It means that the enthalpy change represents the total heat of the system at constant pressure.

$$\Rightarrow dH = TdS + VdP \qquad \ldots (12)$$

Now keeping entropy (S) and pressure (P) constant one by one, we have

$$V = \left(\frac{\partial H}{\partial P}\right)_S \qquad \ldots (13)$$

and $T = \left(\frac{\partial H}{\partial S}\right)_P$ ... (14)

Using $\left(\frac{\partial H}{\partial S\,\partial P}\right) = \left(\frac{\partial H}{\partial P\,\partial S}\right)$, we get $\boxed{\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S}$ ... (15)

3. **Helmholtz function (F) :** If Q amount of heat flows from a single reservoir at a temperature T into a system, the entropy change of the reservoir is

$$(\Delta S)_{\text{res.}} = -\frac{Q}{T} \qquad \ldots (16)$$

By the principle of entropy $(\Delta S)_{\text{system}} + (\Delta S)_{\text{res.}} \geq 0$

$$\Rightarrow S_2 - S_1 - \frac{Q}{T} \geq 0 \quad \left[\because (\Delta S)_{system} = S_2 - S_1\right] \qquad \text{[Since using (16)]}$$

$$\Rightarrow T(S_2 - S_1) \geq Q \qquad \ldots (17)$$

From the first law, when a system performs any process, reversible or irreversible, between two equilibrium states, the work in the process is

$$W = -(U_2 - U_1) + Q \qquad \ldots (18)$$

where $(U_2 - U_1)$ is the change in the internal energy of the system. So, we have

$$W \leq -(U_2 - U_1) + T(S_2 - S_1)$$

$$\Rightarrow W \leq (U_1 - TS_1) - (U_2 - TS_2)$$

Defining $U - TS \equiv F$, the Helmholtz function, we have

$$W \leq F_1 - F_2 \qquad \ldots (19)$$

That is the decrease in the Helmholtz function of a system sets an upper limit to the work in any process between two equilibrium states at the same temperature, during which there is a heat flow into the system from a single reservoir at this temperature.

The equality sign in Eq. (19) holds when the process is reversible and hence the work is maximum. If the process is irreversible, the work is less than this maximum.

Moreover at constant volume $W = PdV = 0$. So, Eq. (19) gives $F_1 - F_2 \geq 0$ or $F_1 \geq F_2$. It means that a process at constant volume and temperature is allowed only if $F_1 \geq F_2$, i.e. Helmholtz function decreases.

Using the definition, $F = U - TS$, we have

$$dF = dU - TdS - SdT$$

$$= TdS - PdV - TdS - SdT \qquad \text{[Since using (2)]}$$

$$\Rightarrow dF = -PdV - SdT \qquad \ldots (20)$$

Keeping volume (V) and temperature (T) constant one by one in Eq. (20), we have

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad \ldots (21)$$

and $$P = -\left(\frac{\partial F}{\partial V}\right)_T \qquad \ldots (22)$$

Differentiating Eq. (21) w.r.t. volume at constant temperature and differentiating Eq. (22) with respect to temperature at constant volume, we have

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \qquad \ldots (23)$$

where we have used $\dfrac{\partial^2 F}{\partial V\,\partial T} = \dfrac{\partial^2 F}{\partial T\,\partial V}$.

4. **Gibbs function (G) :** Consider a process at a constant external pressure P. The PdV work is

$$W = P(V_2 - V_1)$$

If these is non-PdV work (W_{non}) also in the system then from Eq. (19), we have

$$P(V_2 - V_1) + W_{\text{non}} \leq F_1 - F_2$$

$$\Rightarrow W_{\text{non}} \leq (F_1 + PV_1) - (F_2 + PV_2)$$

Writing $F + PV \equiv G$, the Gibbs function, we have

$$W_{\text{non}} \leq G_1 - G_2 \qquad \ldots (24)$$

That is the decrease in the Gibbs function of a system sets an upper limit to the "non-PdV" work in any process between two equilibrium states at the same temperature and pressure. The equality in equation (24) holds when the process is reversible.

Since $G = F + PV$

$\Rightarrow G = U - TS + PV$ ... (25)

where $F = U - TS$

Moreover Eq. (25) gives $G = H - TS$ [Using (11)]

Using Eq. (25), we have

$dG = dU - TdS - SdT + PdV + VdP$

$= TdS - PdV - TdS - SdT + PdV + VdP$ [Since using (2)]

$\Rightarrow dG = -SdT + VdP$ ... (26)

Keeping temperature and pressure (P) constant one by one in Eq. (26), we get

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \text{... (27)}$$

and $$V = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{... (28)}$$

From equations (27) and (28) and exploiting $\left(\frac{\partial^2 G}{\partial P \partial T}\right) = \left(\frac{\partial^2 G}{\partial T \partial P}\right)$, we have

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \quad \text{... (29)}$$

Problem: If U, F, H and G represent internal energy, Helmholtz free energy, enthalpy, and Gibbs free energy respectively, then which one of the following is a correct thermodynamic relation? **[JAM-2016]**

(a) $dU = PdV - TdS$ (b) $dH = VdP + TdS$ (c) $dF = -PdV + SdT$ (d) $dG = VdP + SdT$

CAREER ENDEAVOUR

Soln. The enthalpy is given by

$H = U + PV$

$dH = dU + PdV + VdP$

$\Rightarrow dH = TdS - PdV + PdV + VdP \quad [\because \ dU = TdS - PdV]$

$\Rightarrow dH = TdS + VdP$

Correct option is (b)

Problem: Let U, T, S and P denote, respectively, the internal energy, temperature, entropy and pressure of a thermodynamic system. Then a change ΔF in the free energy $F = U - TS$ measures **[JAM-2009]**

(a) the heat exchanged at constant pressure
(b) the work done by the system at constant entropy
(c) the work done on the system at constant temperature
(d) the heat exchanged at constant temperature

Soln. Given $F = U - TS$

$\Rightarrow \Delta F = \Delta U - T\Delta S - S\Delta T = T\Delta S - P\Delta V - T\Delta S - S\Delta T = -P\Delta V - S\Delta T$

At constant temperature,

$$\Delta F = -P\Delta V$$

So ΔF represents the work done on the system at constant temperature.

Correct option (c)

Problem: A thermodynamic system is maintained at constant temperature and pressure. In thermodynamic equilibrium, its

(a) Gibbs free energy is minimum (b) Enthalphy is maximum

(c) Helmholtz free energy is minimum (d) Internal energy is zero

Soln. The Gibb's free energy is

$$G = U - TS + PV$$

$$\Rightarrow \quad dG = dU - TdS - SdT + PdV + VdP$$

$$= TdS - PdV - TdS - SdT + PdV + VdP$$

$$= -SdT + VdP \qquad [\because \ dU = TdS - PdV]$$

At constant temperature and pressure,

$$dG = 0$$

So Gibbs free energy is minimum.

Correct option is (a)

Problem: The Gibb's function G in thermodynamics is defines as $G = H - TS$ where H is the enthalphy, T is the temperature and S is the entropy. In an isothermal, isobaric, reversible process, value of G

(a) remains constant but not zero (b) varies linearly

(c) varies non linearly (d) is zero

Soln. $G = H - TS = U + PV - TS \qquad [\because \ H = U + PV]$

$$\therefore \quad dG = dU + pdV + VdP - TdS - SdT$$

$$= TdS - PdV + PdV + VdP - TdS - SdT = VdP - SdT$$

In isobaric $(dP = 0)$ and isothermal $(dT = 0)$ process, $dG = 0$

$\Rightarrow$ G remains constant but not zero.

Correct option is (a)

CAREER ENDEAVOUR

Problem: With U and F as thermodynamic potentials, the Gibb's Helmholtz equation is

(a) $U = F - T\left(\frac{\partial F}{\partial T}\right)_V$ (b) $U = F + T\left(\frac{\partial F}{\partial T}\right)_V$ (c) $S = F - T\left(\frac{\partial F}{\partial T}\right)_V$ (d) $S = F + T\left(\frac{\partial F}{\partial T}\right)_V$

Soln. The definition of F is

$$F = U - TS$$

or $U = F + TS$ ... (1)

Also, $dF = dU - TdS - SdT$

$$= TdS - PdV - TdS - SdT = -PdV - SdT$$

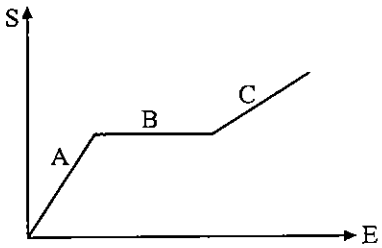
$$\therefore \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad \text{... (2)}$$

Using equation (2) in (1),

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

Correct option is (a).

Problem: The entropy S of a thermodynamic system as a function of energy E is given by the following graph-



The temperatures of the phases A, B and C, denoted by T_A, T_B and T_C, respectively, satisfy the following inequalities :

(a) $T_C > T_B > T_A$ (b) $T_A > T_C > T_B$ (c) $T_B > T_C > T_A$ (d) $T_B > T_A > T_C$

Soln. We know that,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

From figure,

$$\left(\frac{\partial S}{\partial E}\right)_A > \left(\frac{\partial S}{\partial E}\right)_C > \left(\frac{\partial S}{\partial E}\right)_B$$

$\Rightarrow \quad T_B > T_C > T_A$

Correct option is (c)

Problem: The internal energy E of a system is given by $E = \frac{bS^3}{VN}$, where b is a constant and other symbols have their usual meaning. The temperature of this system is equal to

(a) $\frac{bS^2}{VN}$ (b) $\frac{3bS^2}{VN}$ (c) $\frac{bS^3}{V^3N}$ (d) $\left(\frac{S}{N}\right)^2$

Soln. We know that,

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$$

Where $E = \frac{bS^3}{VN}$ $\quad \therefore \quad T = \frac{3bS^2}{VN}$

Correct option is (b)

Problem : Let U, T, S and P denote, respectively, the internal energy, temperature, entropy and pressure of a thermodynamic system. Then a change ΔF in the free energy $F = U - TS$ measures

(a) the heat exchanged at constant pressure
(b) the work done by the system at constant entropy
(c) the work done on system at constant temperature
(d) the heat exchanged at constant temperature

[JNU : 2009]

Soln. $F = U - TS$

$dF = dU - TdS - SdT$

$= TdS - PdV - TdS - SdT$

$= - PdV - SdT$

At constant temperature, $dF = - PdV$

So, ΔF measures the work done by system at constant temperature.

Hence, correct option is (c)

Maxwell Equations

The equations (7), (15), (23) and (29) are called Maxwell equations. They are :

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V ; \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P ; \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V ; \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Note :

1. In each of the Maxwell relations, the cross product of the differentials has the dimensions of energy.

2. The independent variable in the denominator of one side of an equation is the constant on the other side.

Problem: Establish the following thermodynamic relation $\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha$ where α in the coefficient of volume expansion at constant pressure. Hence, show that increase in pressure heats a body that expands with rise of temperature and colds that contracts on heating.

Soln. The Maxwell thermodynamic relation is:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying by T both side

$$T\left(\frac{\partial S}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow \quad \left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P \qquad (\because dQ = TdS)$$

$$\Rightarrow \quad \left(\frac{\partial Q}{\partial P}\right)_T = -TV\frac{I}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow \quad \left(\frac{\partial Q}{\partial P}\right)_T = -TV\alpha \qquad \text{where} \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P - \text{Coefficient of Volume expansion}$$

(i) If substance expands with rise in temperature then α will be positive

Hence, $\left(\frac{\partial Q}{\partial P}\right)_T < 0$

If we increase the pressure, ∂Q at constant temperature will be negative. So, to maintain temperature constant heat must be drawn from the system. It means increase in pressure will heat the system.

(ii) If substance contracts with rise in temperature then α will be negative. Hence,

$$\left(\frac{\partial Q}{\partial P}\right)_T = +Ve$$

If we increase the pressure $(\partial Q)_T$ will be positive, to maintain temperature constant heat must be given to the system. It means increase in pressure will cools the system.

Problem: Show that $\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = 0$

where α and β are the coefficient of thermal expansion and coefficient of compressibility respectively

Soln. Since V is a state function so we can write

$$\frac{\partial^2 V}{\partial T \partial P} = \frac{\partial^2 V}{\partial P \partial T} \quad \text{or} \quad \frac{\partial}{\partial T}(-V\beta)_P = \frac{\partial}{\partial P}(V\alpha)_T \qquad \left[\because -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \beta \text{ and } \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha\right]$$

Carrying out the differentiation we get

$$-\beta\left(\frac{\partial V}{\partial T}\right)_P - V\left(\frac{\partial \beta}{\partial T}\right)_P = \alpha\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial \alpha}{\partial P}\right)_T$$

or $$-\frac{\beta}{V}\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial \beta}{\partial T}\right)_P = \frac{\alpha}{V}\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial \alpha}{\partial P}\right)_T$$

$$\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\alpha\beta}{\partial T}\right)_P = -\frac{\beta}{V}\left(\frac{\partial V}{\partial T}\right)_P - \frac{\alpha}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$= -\frac{\beta}{V}(\alpha V) - \frac{\alpha}{V}(-\beta V) = 0$$

Energy Equation

First law of thermodynamics $\Rightarrow$ $dQ = dU + PdV$

Second law of thermodynamics $\Rightarrow$ $dQ = T\,dS$

Combining these two laws $\Rightarrow$ $TdS = dU + PdV$

This equation is called combined first and second law of thermodynamics.

$$\Rightarrow \quad dS = \frac{1}{T}dU + \frac{P}{T}dV$$

CAREER ENDEAVOUR

Differentiate w.r.t. volume at constant temperature, we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} \quad \Rightarrow \quad T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P$$

Using Maxwell's thermodynamic relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ the above equation become

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T + P$$

So, $$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \qquad \ldots (30)$$

This relation is called *Energy equation*.

(i) For an ideal gas:

The equation of state for an ideal gases is

$$PV = RT \Rightarrow P = \frac{RT}{V} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

Put this value in equation (30), we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T.\frac{R}{V} - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0 \left(\because \frac{RT}{V} = P\right)$$

Hence internal energy of an ideal gas is independent of volume

(ii) For a vander Waal gas (or Perfect gas) :

The equation of state is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

Putting this value in equation (30), we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T.\frac{R}{V - b} - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

Hence internal energy of an real gas depends on volume.

Problem: A gas obeys the equation of state $PV = nRT + nB(T)P$, where $B(T)$ is a constant which depends on temperature. Find W, ΔU, Q and ΔH.

Soln. Here $W = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{RT}{V - B} dV = -RT \ln\left(\frac{V_2 - B}{V_1 - B}\right)$, $W = RT \ln\left(\frac{P_2}{P_1}\right)$

Now, $dU = TdS - PdV$,

The energy equation is $\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$

We know, $\Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \left[-P + T\left(\frac{\partial P}{\partial T}\right)_V\right] dV$

Here, $P = \frac{RT}{V - B}$

or $\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{V-B} + \frac{RT}{(V-B)^2}\frac{dB}{dT}$

$\therefore \quad T\left(\frac{\partial P}{\partial T}\right)_v = \frac{RT}{V-B} + \frac{RT^2}{(V-B)^2}\frac{dB}{dT}$

Hence $\Delta U = RT^2 \frac{dB}{dT}\int_{V_1}^{V_2} \frac{dV}{(V-B)^2} = -RT^2 \frac{dB}{dT}\left(\frac{1}{V_2-B} - \frac{1}{V_1-B}\right) = -T\frac{dB}{dT}\left(\frac{RT}{V_2-B} - \frac{RT}{V_1-B}\right)$

Or, $\boxed{\Delta U = T\frac{dB}{dT}(P_1 - P_2)}$

To calculate Q, we use first law so

$Q = \Delta U - W \quad \Rightarrow Q = T\frac{dB}{dT}(P_1 - P_2) + RT\ln\left(\frac{P_1}{P_2}\right)$

For ΔH, $\Delta H = \Delta U + \Delta(PV)$

$\Rightarrow \Delta(PV) = \Delta(RT + BP) = (RT + BP_2) - (RT + BP_1) = B(P_2 - P_1)$

Hence $\Delta H = T\frac{dB}{dT}(P_1 - P_2) + B(P_2 - P_1)$

or $\boxed{\Delta H = \left(B - T\frac{dB}{dT}\right)(P_2 - P_1)}$

Problem: A certain gas obeys the equation of state $P(V-b) = RT$

(i) Derive an expression for heat & work in a reversible isothermal expansion of the gas

(ii) Derive an expression for heat & work in a reversible adiabatic expansion of the gas

(iii) Calculate ΔU, Q and W when 1 mol of the gas expands reversible at 300K from 0.220 to 20.02 litre.

(a) isothermally (b) adiabatically. Assume that b = 0.020 litre mol^{-1}, $C_V = \frac{3}{2}R$ and $\gamma = \frac{5}{3}$

Soln. (i) $dW = PdV$ or $W = \int_{V_1}^{V_2} PdV$

Given equation of state is $P = \frac{RT}{(V-b)}$

Thus, $W = \int_{V_1}^{V_2} \frac{RT}{V-b}dV = RT\ell n\left(\frac{V_2-b}{V_1-b}\right)$

Now, $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{\partial\left(\frac{RT}{V-b}\right)}{\partial T}\right)_V - P$

$= \frac{RT}{V-b} - P = P - P = 0$

$\Rightarrow \quad \Delta U = 0$

Thus, $Q = \Delta U + W = W = RT\,\ell n\left(\frac{V_2 - b}{V_1 - b}\right)$

(ii) For adiabatic reversible expansion, Q = 0

Hence $dU = dW = \frac{RT}{V-b}dV$

$$\Rightarrow \int_{T_1}^{T_2}\frac{C_V dT}{T} = \int_{V_1}^{V_2}\frac{R}{V-b}dV \Rightarrow C_V \ell n\left(\frac{T_2}{T_1}\right) = R\ell n\left(\frac{V_2-b}{V_1-b}\right)$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_2-b}{V_1-b}\right)^{\frac{R}{C_V}} = \left(\frac{V_2-b}{V_1-b}\right)^{(\gamma-1)}$$

$$\therefore W = \Delta U = C_V\left(T_2 - T_1\right)$$

$$= C_V T_1\left[\left(\frac{V_1-b}{V_2-b}\right)^{\gamma-1} - 1\right]$$

(iii) $T_1 = T_2 = 300K, V_1 = 0.220$ litre, $V_2 = 20.020$ litre, $b = 0.020$ litre mol^{-1}

(a) For isothermal reversible expansion

$$W = Q = RT_1\ \ell n\left(\frac{V_2-b}{V_1-b}\right) = (8.314)(300)\,\ell n\left(\frac{20.0}{0.20}\right) = 11.548\ KJ\ mol^{-1}$$

$\Delta U = 0$

(b) For an adiabatic reversible expansion

$Q = 0$ thus

$$\Delta U = W = C_V T_1\left[\left(\frac{V_1-b}{V_2-b}\right)^{\gamma-1} - 1\right]$$

Given, $C_V = \frac{3}{2}R$, $\gamma = \frac{5}{3}$ and $T_1 = 300\ K$

$$\Delta U = W = \left(\frac{3}{2}R\right)(300)\left[\left(\frac{200}{20000}\right)^{2/3} - 1\right] = -3.554 \text{ kJ}$$

General Relation between C_V and C_P

The specific heat at constant pressure and constant volume are given as

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad [\because dQ = TdS]$$

and $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$

Now, if the entropy S is regarded as a function of T and V and since dS is perfect differential

$S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

From Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\therefore \quad T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Now, $$C_P - C_V = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(31)$$

(a) For a perfect gas

The equation of state is $PV = RT$.

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$\therefore \quad C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T\left(\frac{R}{V}\right)\left(\frac{R}{P}\right) = \frac{TR^2}{PV} = \frac{R^2T}{RT} = R$$

(b) For a vander Waal's gas

The equation of state is $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

or $$\left(P + \frac{a}{V^2}\right) = \frac{RT}{V - b} \quad \ldots(32)$$

where a and b are constant

Differentiating equation (32) w.r.t. T at constant volume, we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

Differentiating equation(32) w.r.t. T at constant pressure ,we get

$$0 - \frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{R}{V-b}$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P \left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right] = \frac{R}{V-b} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{\frac{R}{V-b}}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right]}$$

Substituting the value of $\left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial V}{\partial T}\right)_P$ in equation (31) we have

$$C_P - C_V = T\frac{R}{V-b}\cdot\frac{\frac{R}{V-b}}{\left[\frac{RT}{(V-b)^2}-\frac{2a}{V^3}\right]} = \frac{R^2T}{(V-b)^2}\frac{1}{\left[\frac{RT}{(V-b)^2}-\frac{2a}{V^3}\right]}$$

So $$C_P - C_V = \frac{R}{1-\frac{2a}{V^3}\frac{(V-b)^2}{RT}}$$

Neglecting b in comparison to V

$$C_P - C_V = \frac{R}{1-\frac{2a}{V^3}\frac{V^2}{RT}} = \frac{R}{1-\frac{2a}{RTV}} = R\left(1-\frac{2a}{RTV}\right)^{-1}$$

Expanding binomially and neglecting higher powers we get

$$C_P - C_V = R\left(1+\frac{2a}{RTV}\right)$$

TdS Eequations

(i) $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$ (ii) $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

Prove :

(i) Let the entropy S of a thermodynamic system be a function of temperature T and volume V i.e. $f(T, V)$. Since dS is a perfect differential, so we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying by T, we have

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \quad \ldots (33)$$

Since $TdS = dQ$ and for any substance the specific heat at constant volume is given by

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

From Maxwell's equation, we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Making these substitution in equation (33), we get

$$\boxed{TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV}$$ which is the required relation

(ii) Let the entropy S of a thermodynamic system be function of temperature T and pressure P i.e., $S=f(T,P)$
Since dS is a perfect differential

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying by T, we get

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \quad \ldots (34)$$

For any substance the specific heat at constant pressure is given by

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

From Maxwell's equation, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Making these substitution in equation (34), we get

$$\boxed{TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP}$$

PROBLEMS TO BE PLAYED

1. Which of the following is not Maxwell's thermodynamic relation?

(a) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (b) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ (c) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ (d) $\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial S}{\partial T}\right)_V$

2. Which of the following Maxwell's relation leads of Clausius–Clapeyron equation?

(a) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial T}\right)_V$ (b) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (c) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ (d) $\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$

3. The thermodynamical relation expressing the change at temperature with volume at constant entropy is–

(a) $\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial Q}\right)_V$ (b) $\left(\frac{\partial T}{\partial V}\right)_S = T\left(\frac{\partial P}{\partial Q}\right)_V$

(c) $\left(\frac{\partial T}{\partial V}\right)_S = -V\left(\frac{\partial P}{\partial Q}\right)_T$ (d) $\left(\frac{\partial T}{\partial V}\right)_S = T\left(\frac{\partial P}{\partial Q}\right)_T$

4. The thermodynamical relation expressing T*d*S equation–

(a) $TdS = C_V dT - T\left(\frac{\partial P}{\partial T}\right)_V dV$ (b) $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

(c) $TdS = C_V dT - T\left(\frac{\partial S}{\partial V}\right)_T$ (d) $TdS = C_V dT + T\left(\frac{\partial S}{\partial V}\right)_T$

5. The Gibb's function G in thermodynamics is defined as

$$G = H - TS$$

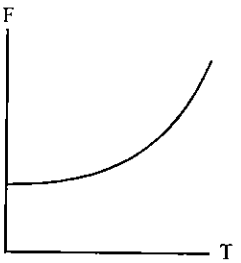
(where H = Enthalpy, T = Temperature, S = Entropy)
In an isothermal, isobaric, reversible process, G

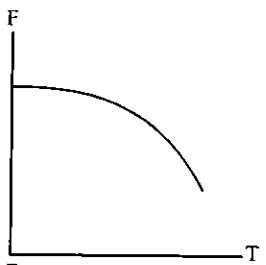
(a) Remains constant but not zero (b) Varies linearly
(c) Varies non linearly (d) Is zero

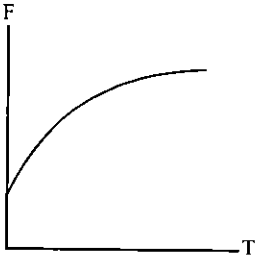
6. The Gibb's potential is defined as–

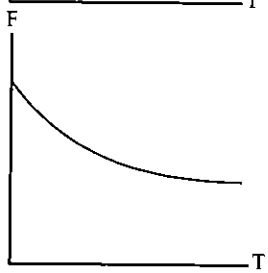
(a) $G = U - PV + TS$ (b) $G = U + PV + TS$
(c) $G = U - PV - TS$ (d) $G = U + PV - TS$

7. For a stable thermodynamics system, the temperature dependence of the free energy $F(T)$ is represented by

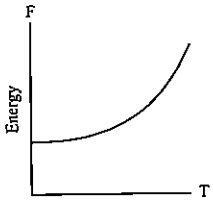
(a) 

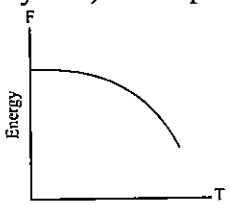
(b) 

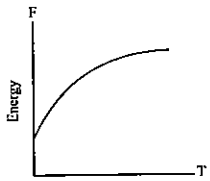
(c) 

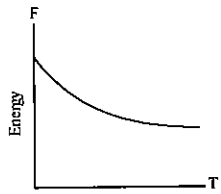
(d) 

8. For a stable thermodynamic system, the temperature dependence of the internal energy U(T) is represented as

(a) 

(b) 

(c) 

(d) 

9. With U and F as thermodynamic potentials, the Gibb's Helmholtz equation is given as

(a) $U = F - T\left(\frac{\partial F}{\partial T}\right)_V$ (b) $U = F + T\left(\frac{\partial F}{\partial T}\right)_V$ (c) $S = F - T\left(\frac{\partial F}{\partial T}\right)_V$ (d) $S = F + T\left(\frac{\partial F}{\partial T}\right)_V$

10. A fluid at high pressure is throuttled through a narrow porous opening in a region of lower pressure without any transfer of heat. In such a process

(a) The entropy does not change
(b) The Gibb's free energy remains constant
(c) The entropy is decreased
(d) The enthalpy of the fluid is constant

11. Which of the following is not an exact differential?

(a) dQ (Q = heat absorbed)
(b) dU (U = internal energy)
(c) dS (S = entropy)
(d) dF (F = free energy)

ANSWER KEY

1. (d)	**2. (b)**	**3. (a)**	**4. (b)**	**5. (a)**	**6. (d)**	**7. (a)**
8. (b)	**9. (a)**	**10. (d)**	**11. (a)**			

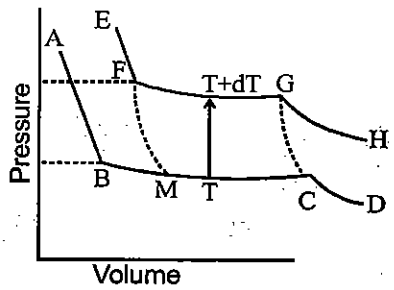
Chapter 6

The Phase Transition

Clausius Clapeyron Equation

The phase diagram shows that only two phase of water co-exist at a time, either liquid and gas or solid and liquid or solid and gas. When there is change in the states from solid to liquid state, the characteristic temperature is called the *melting point* of solid and when it is from liquid to vapour the temperature is called *boiling point* of the liquid.

Clausius developed the relation which shows the variation in the boiling and melting with the pressure by applying II law of thermodynamics that relation is known as *Clausius Clapeyron equation.*



ABCD and EFGH are two isothermals which are maintained at infinitesimally close temperature T and T+dT. In figure AB and EF represents the liquid state of the substance. At point B and F, substance exists in pure liquid state. FG and BC are that states where liquid and vapour phase of the substance co-exist. Substance is purely in vapour state in GH and CD states.

In order to form a Carnot cycle, we draw two adiabatic from F and G to M and C respectively. Now, FGCMF forms a Carnot cycle in which FG represents the isothermal expansion, GC shows the adiabatic expansion, NM is the process along which isothermal boiling point of liquid rises with increase in pressure and vice versa. The amount of heat Q_1 absorbed along FG is equal to the latent heat of vapourization (L + dL) at temperature (T + dT) as substance changing from liquid state at F to the vapourization state FG. From C to B, the amount of heat rejected is Q_2. Here, Q_2 is equal to the latent heat of vapourization L at temperature T. By increasing the pressure a little, the original point F is restored. So, the cycle FGCBF is completely reversible. Then applying the principle of Carnot's reversible cycle, we have

From the Carnot cycle.

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_1}$$

$$\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$$

Since, $Q_1 = L + dL \;\&\; Q_2 = L$

Also, $T_1 = T + dT \;\&\; T_2 = T$

Then $\frac{L+dL-L}{L}=\frac{T+dT-T}{T}$

$$dL=\frac{L}{T}dT \quad \ldots(1)$$

The amount of heat converted into work $=Q_1-Q_2=L+dL-L=dL \quad \ldots(2)$

The work done by the substance is also represented by the area under curve, i.e. area of rhombus.

$$dL=dP(V_2-V_1) \quad \ldots(3)$$

Using equation (1), (2) and (3)

We have $\frac{L}{T}dT=dP(V_2-V_1) \Rightarrow \boxed{\frac{dP}{dT}=\frac{L}{T(V_2-V_1)}}$

This equation is called *Clausius–Clapeyron Equation*. This is true for both the change of state, i.e., from liquid to vapour and solid to liquid.

1. **Effect of melting point:**

When solid melts, there occurs two cases.

(a) When $V_2 > V_1$ for substance like wax, sulphur, $\frac{dP}{dT}>0$, therefore melting point of solid rise with rise in pressure and vice versa.

(b) When $V_2 < V_1$ for substance like ice, gallium and bismuth, V_2-V_1 is negative quantity. Hence $\frac{dP}{dT}$ is also negative, which means melting point of such substance decreases with increase in pressure.

2. **Effect of pressure on boiling points of liquid.**

When liquid boil i.e. changes its state from liquid to gaseous, there is an increase in volume, which means (V_2-V_1) is positive and hence $\frac{dP}{dT}>0$.

Problem: The pressure versus temperature diagram of a given system at certain low temperature range is found to be parallel to the temperature axis in the liquid to solid transition region. The change in the specific volume remains constant in this region. The conclusion one can get from the above is

(a) the entropy of solid is zero in this temperature region

(b) the entropy increases when the system goes from liquid to solid phase in this temperature region

(c) the entropy decreases when the system transforms from liquid to solid phase in this region

(d) the change in entropy is zero in the liquid to solid transition region

Soln. *P-T* curve is parallel to the temperature axis

$\Rightarrow$ slope of the curve = 0

$$\Rightarrow \frac{dP}{dT}=0 \quad \ldots(i)$$

Now, from Clausius-Clapeyron equation

$$\frac{dP}{dT}=\frac{L}{T\Delta V}=\frac{\Delta S}{\Delta V} \quad \left[\because \Delta S=\frac{L}{T}\right] \quad \ldots(ii)$$

We know $\frac{dP}{dT}=\frac{\Delta S}{\Delta V}$

Therefore, from (i), $\Delta S = 0$.

Hence, the correct option is (d).

Problem: A solid melts into a liquid via first order phase transition. The relationship between the pressure P and the temperature T of the phase transition is $P = -2T + P_0$, where P_0 is a constant. The entropy change associated with the phase transition is 1.0 J mole^{-1} K^{-1}. The Clausius Clapeyron equation for the latent heat is $L = T\left(\frac{dP}{dT}\right)\Delta V$. Here, $\Delta V = V_{liquid} - V_{solid}$ is the change in molar volume at the phase transition. The correct statement relating the values of the volumes is

(a) $V_{liquid} = V_{solid}$ (b) $V_{liquid} = V_{solid} - 1$ (c) $V_{liquid} = V_{solid} - 1/2$ (d) $V_{liquid} = V_{solid} + 2$

[IIT-JAM : 2006]

Soln. $P = -2T + P_0$

$$\frac{dP}{dT} = -2$$

Entropy changes $\Delta S = \frac{L}{T} = 1$ (Given)

From Clausius Clapeyron equation, $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$, we have

$$\Delta V = V_{liquid} - V_{solid} = -\frac{1}{2}$$

So, $V_{liquid} = V_{solid} - \frac{1}{2}$

Correct option is (c)

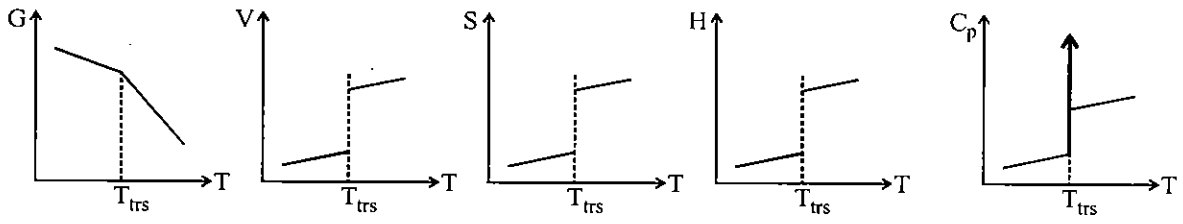
Phase Transition

The term phase transition is most commonly used to describe transitions between solid, liquid and gaseous states of matter, and, in rare cases, plasma. A phase of a thermodynamic system and the states of matter have uniform physical properties. During a phase transition of a given medium certain properties of the medium change, often discontinuously, as a result of the change of some external condition, such as temperature, pressure, or others. For example, a liquid may become gas upon heating to the boiling point, resulting in an abrupt change in volume. The measurement of the external conditions at which the transformation occurs is termed the *phase transition.*

Types of phase transition

(1) First order phase transition

- The change in phase, in which heat is either absorbed or released and occured at constant temperature and pressure are known as *first order phase transition.*
- The Gibb's function G remains constant in both phases at transition point.
- The first derivative of G with respect to temperature, i.e., entropy and with respec) pressure, i.e., volume (or density) is discontinuous at transition point.
- The examples are transformation of liquid into vapour and solid into liquid.
- The graphs are :



where $\left(\frac{\partial G}{\partial T}\right)_P = -S$, $\left(\frac{\partial G}{\partial P}\right)_T = V$

- $(\Delta G)_{\text{trans.}} = 0$

  $(\Delta S)_{\text{trans.}} = \frac{\Delta H_{\text{trans.}}}{T_{\text{trans.}}} \neq 0$

- $(\Delta V)_{\text{trans.}} \neq 0$

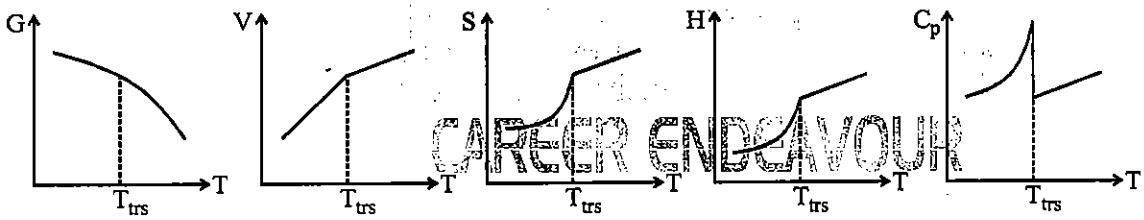
(2) The Second Order Phase Transition

- The first derivative of Gibb's function with respect to temperature and pressure are continuous at transition point, i.e., entropy and volume respectively in second order phase transition.
- So $S = -\left(\frac{\partial G}{\partial T}\right)_P$ and $V = \left(\frac{\partial G}{\partial P}\right)_T$ are continuous at the transition point.
- The second derivatives with respect to temperature and pressures are discontinuous.

  i.e., $\left(\frac{\partial^2 G}{\partial T \partial P}\right) = \left(\frac{\partial V}{\partial T}\right)_P = \alpha V$ and $\left(\frac{\partial^2 G}{\partial P \partial T}\right) = -\left(\frac{\partial S}{\partial T}\right)_T = \frac{-C_V}{T}$ are discontinuous

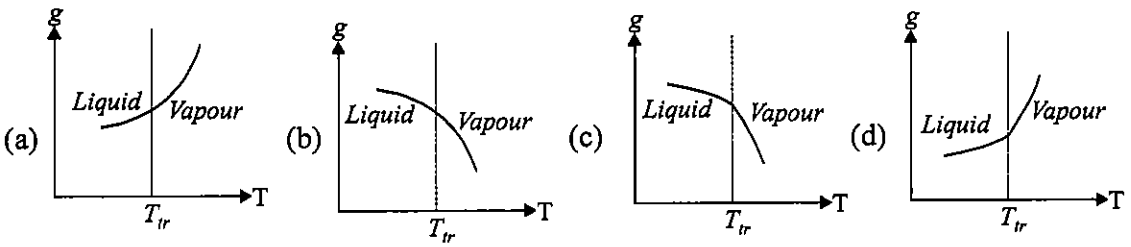
Note : C_P is also discontinuous at transition point.

- It means that the coefficient of isothermal compressibility (α) and specific heat at constant volume, (C_V) or at constant pressure (C_P) at transition point are discontinuous and have different values in different phases.
- For example, liquid-vapour transition at the critical point, the transition of a super-conductor from the superconducting to the normal state in zero magnetic field, ferromagnetic to paramagnetic transitions in simple model etc.
- The Graphs are:



CAREER ENDEAVOUR

Problem: For a liquid to vapour phase transition at T_{tr}, which of the plots between specific Gibbs free energy 'g' and temperature 'T' is correct?



[IIT-JAM : 2012]

Soln. **(c)** Actually, variation of g with T is determined by the entropy. Because the entropy of gaseous phase of substance is greater than that of liquid phase. Therefore, *g* for gas changes more steeply than that for liquid.

Problem: A thermodynamic system is maintained at constant temperature and pressure. In thermodynamic equilibrium, its **[IIT-JAM : 2008]**

(a) Gibbs free energy is minimum
(b) Enthalpy is maximum
(c) Helmholtz free energy is minimum
(d) Internal energy is zero

Soln. The Gibb's free energy is $G = U - TS + PV$

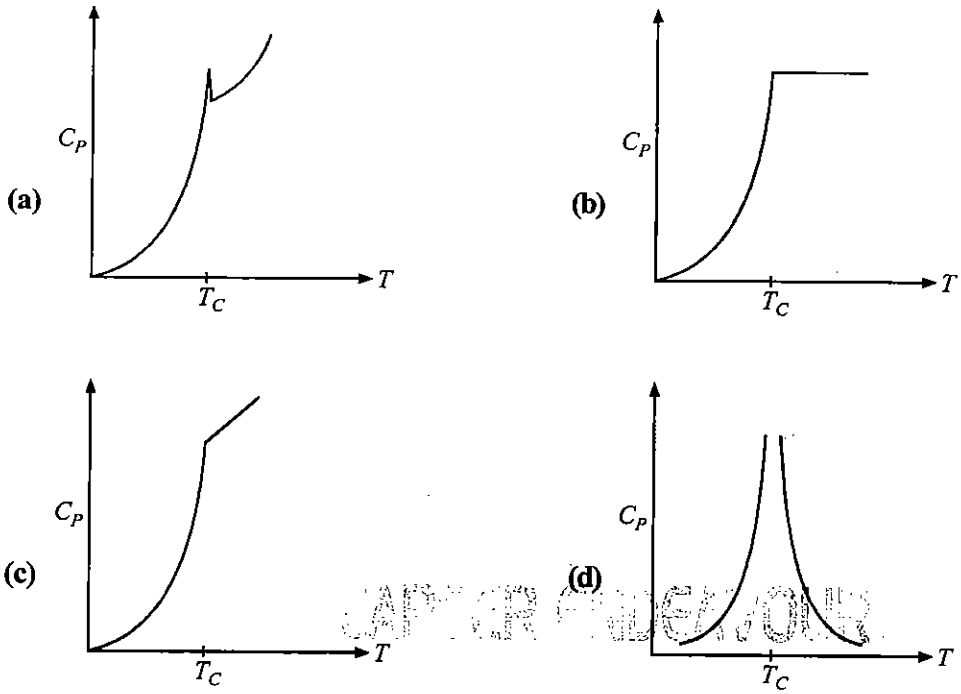
$\Rightarrow \quad dG = dU - TdS - S\,dT + PdV + VdP = -SdT + VdP$

At constant T and P, $dG = 0$

So, G is minimum.

Correct option is (a)

Problem: The plot of specific heat versus temperature across the superconducting transition temperature (T_C) is most appropriately represented by



Soln. Phase transition for superconducting state is a second order phase transition. For second order phase transition the C_P has a finite discontinuity at the transition temperature.

Hence correct option is (a).

Problem: In a first order phase transition, at the transition temperature, specific heat of the system

(a) diverges and its entropy remains the same
(b) diverges and its entropy has finite discontinuity
(c) remains unchanged and its entropy has finite discontinuity
(d) has finite discontinuity and its entropy diverges

Soln. The key points are:

(i) specific heat diverges for both first and second order phase transitions.
(ii) The entropy has a finite discontinuity only for first order phase transition is continuous for second order phase transition.

Keeping the above key points in mind, we can see that correct answer is (b).

Hence, the correct option is (b).

Problem: Across a first order phase transition, the free energy is
(a) proportional to the temperature
(b) a discontinuous function of the temperature
(c) a continuous function of the temperature but its first derivative is discontinuous
(d) such that the first derivative with respect to temperature is continuous

Soln.

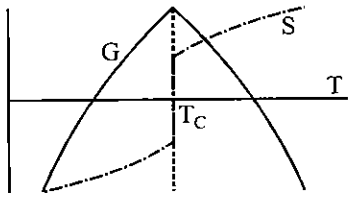


Figure : Schematic diagram for the Gibbs free energy and the entropy in a first order phase transition.

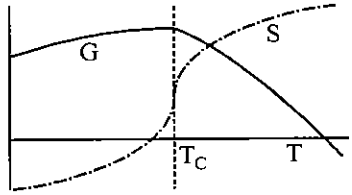


Figure : Schematic diagram for the Gibbs free energy and the entropy in a continuous phase transition.

From the above we can see that for first order transition the Gibbs free energy is itself continuous function of temperature but at the transition temperature there is a discontinuity in its first derivative withrespect to temperature i.e., entropy.
Hence correct option is (c).

Problem: Identity which one is a first order phase transition?
(a) A liquid to gas transition at its critical temperature
(b) A liquid to gas transition close to its triple point
(c) A paramagnetic to ferromagnetic transition in the absence of a magnetic field
(d) A metal to superconductor transition in the absence of a magnetic field

Soln. Clearly option (c) and (d) are not first order phase transition as it involves symmetry variation. So now the confusion can arise only with option (a) and (b). In order to avoid that confusion, the key point is the definition of critical point. Beyond the critical point, no phase transition is possible, therefore it cannot be the right answer.
Hence, the correct option is (b).

Problem: Which one of the following is a first order phase transition?
(a) Vaporization of a liquid at its boiling point
(b) Ferromagnetic to paramagnetic
(c) Normal liqiuid He to superfluid He
(d) Superconducting to normal state

Soln. Vaporization of a liquid at its boiling point, in which only phase is changed, is the first order phase transition but in other three options, the structure of material is changed, so these are second order phase transition.
Hence correct option is (a).

Problem: Consider the transition of liquid water to steam as water boils at a temperature of 100°C under a pressure of 1 atmosphere. Which one of the following quantities does not change discontinuously at the transition?

(a) The Gibbs free energy (b) The internal energy
(c) The entropy (d) The specific volume

Soln. Liquid water to steam is first order phase transition. So, G is continuous and I order derivative of G is discontinuous.

$\therefore \quad \left(\frac{dG}{dP}\right)_T = V$ is discontinuous.

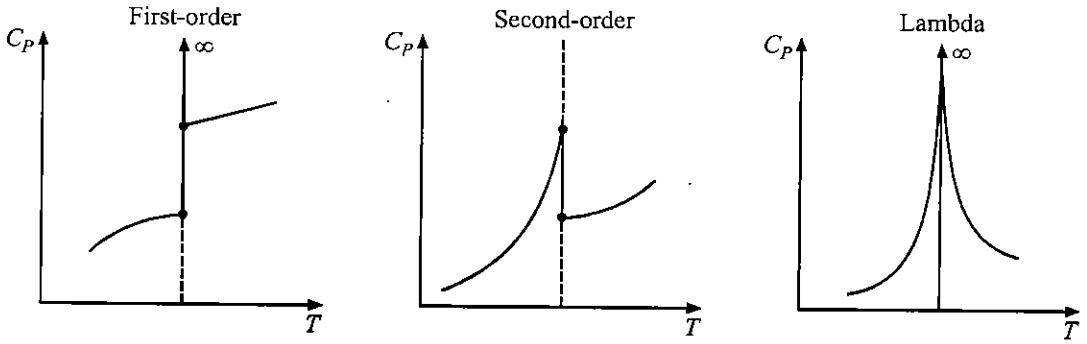
$\therefore \quad -\left(\frac{dG}{dT}\right)_P = S$ is discontinuous.

$U = G + TS - PV$ is also discontinuous.

Correct answer : (a)

Problem: A second order phase transition is one in which
(a) the plot of entropy as a function of temperature shows a discontinuity
(b) the plot of volume heat as a function of temperature shows a discontinuity
(c) the plot of volume as a function of pressure shows a discontinuity
(d) the plot of comprehensility as a function of temperature is continuous

Soln.

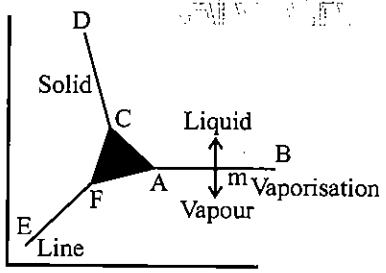


(a) **(b)** **(c)**

Distinguish characteristics among the three types of phase transitions: (a) first order; (b) second order; (c) lambda.

Hence correct option is (b).

Triple Point



In the figure AB represent the vaporisation state.
If at point m, pressure is increased keeping temperature constant then boiling point will increase and all vapour condense into liquid line. CD represents the ice line or fusion line separating solid and liquid phase of water. Line EF indicates when the pressure on ice is raised evaporation from its surface slows down. The equilibrium between solid and vapour state of a substance can be represented by a curve CD called *sublimation line.* All the state of water co-exist only at the triple point state.

Problem: The vapour pressure p (in mm of Hg) of a solid, at temperature T, is expressed by $\ell n\ p = 23 - 3863/T$ and that of its liquid phase by $\ell n\ p = 19 - 3063/T$. The triple point (in Kelvin) of the material is:
(a) 185 (b) 190 (c) 195 (d) 200

Soln. At triple point the vapour pressure of solid and liquid phases are equal.

Hence, $23 - \frac{3863}{T} = 19 - \frac{3063}{T}$

$\Rightarrow 4 - \frac{3863}{T} = -\frac{3063}{T}$

$\Rightarrow 4T - 3863 = -3063 \Rightarrow 4T = 3863 - 3063$

or $4T = 800$

$T = 200$ K

Hence correct option is (d).

CAREER ENDEAVOUR

PROBLEMS TO BE PLAYED

1. Using second latent heat equation $C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$ show that the specific heat of steam is negative–
(a) If L = 800 – 0.705 T (b) If L = 800 T – 0.705
(c) If L = 800 T^2 – 0.705 T (d) If L = 800 T 0.705 T^2

2. The Clausius-Clapeyron equation indicates that an increase in pressure increases the melting point, in case of–
(a) All substances
(b) Substances which expand on solidification
(c) Substances which contract on solidification
(d) Substances which neither expand nor contraction on solidification

3. When a liquid is heated but its state remains unchanged, its molecule gain–
(a) P. E. (b) K.E. (c) Both (a) & (b) (d) None of these

4. In the process of phase transition–
(a) Gibb's potential function remains constant–
(b) Only entropy remains constant
(c) Only volume remains constant
(d) Only temperature remains constant

5. A second order phase transition is characterised by–
(a) A latent heat
(b) A discontinuous change in specific heat
(c) A change in volume
(d) Irreversible behaviour during warming and cooling

6. At the critical point
(1) The difference in densities of the liquid and gaseous phase is small
(2) The pressure does not depend on the volume
(3) Density fluctuations are large
(4) The latent heat for liquid vapour transition becomes very large
(a) 1 Only (b) 2 and 3 (c) 3 and 4 (d) 4 Only

7. A second order phase transition is one in which–
(a) The plot of entropy as a function of temperature shows a discontinuity
(b) The plot of specific heat as a function of temperature shows a discontinuity
(c) The plot of volume as a function of pressure shows a discontinuity
(d) The plot of comprehensibility as a function of temperature is continuous

8. At the critical point
1. difference in densities of the liquid and gaseous phase is small
2. pressure does not depend on the volume
3. density fluctuations are large
4. latent heat for liquid-vapour transition becomes very large.
(a) 1 only (b) 2 and 3 (c) 3 and 4 (d) 4 only

ANSWER KEY

1. (a) 2. (c) 3. (a) 4. (a) 5. (b) 6. (a) 7. (a)

8. (b)

Chapter 7

Statistical Mechanics

Fundamental Concepts and Theorems

- **The macroscopic and microscopic states**

We consider a physical system composed of N identical particles confined to a space of volume V. Next we consider the total energy of the system is E.

The specification of the actual values of the parameters N, V and E then define a *macrostate* of the given system.

At the molecular level, however a large number of possibilities still exist because at that level there will in general be a large number of different ways in which the macrostate (N, V, E) of the given system can be realized. In other words there will be a large number of different ways in which the total energy E of the system can be distributed among N particles constituting it. Each of these (different) ways specifies a *microstate.*

- **Equal a priori probabilities theorem**

In any case to a given macrostate of the system there does in general correspond a large number of microstates and it seems natural to assume when there are no constraints, then at any time t the system is equally likely to be in any one of these microstates. This assumption forms the backbone of our formalism and is generally referred to as the postulate of "*equal a priori probabilities*" for all microstates consistent with the given macrostate.

- **The ensemble theory**

We noted that, for a given macrostate (N, V, E), a statistical system, at any time t, is equally likely to be in any one of an extremely large number of distinct microstates. As time passes, the system continually swtiches from one microstate to another, with the result that, over a reasonable span of time, all one observes is a behavior "averaged" over the variety of microstates through which the system passes. It may, therefore, make sense if we consider, at a single instant of time, a rather large number of system-all being some sort of "mental copies" of the given system-which are characterized by the same macrostate as the original system but are, naturally enough in all sorts of possible microstates. Then, under ordinary circumstances, we may expect that the average behavior of any system in this collection, which we call an ensemble, would be identical with the time-averaged behavior of the given system. It is on the basis of this expectation that we proceed to develop the so-called ensemble theory.

For classical systems, the most appropriate workshop for developing the desired formalism is the phase space.

- **Phase Space**

The microstate of a given classical system, at any time t, may be defined by specifying the instantaneous positions and momenta of all the particles constituting the system. Thus, if N is the number of particles in the system, the definition of a microstate requires the specification of $3N$ position coordinates $q_1, q_2, \ldots, q_{3N}$ and $3N$ momentum coordinates $p_1, p_2, \ldots, p_{3N}$. Geometrically, the set of coordinates (q_i, p_i) where $i = 1, 2, \ldots, 3N$, may be regarded as a point in a space of $6N$ dimensions. We refer to this space as the *phase space*, and the phase point (q_i, p_i) as a representative point, of the given system.

Of course, the coordinates q_i and p_i are functions of the time t; the precise manner in which they vary with time t is determined by the canonical equations of motion, where $H(q_i, p_i)$ is the Hamiltonian of the system.

Now, as time passes, the set of coordinates (q_i, p_i), which also defines the microstate of the system, undergoes a continual change. Correspondingly, our representative point in the phase space carves out a trajectory.

Problem: The dimension of phase space of ten rigid diatomic molecules is:
(a) 5 (b) 10 (c) 50 (d) 100

Soln. A rigid diatomic molecule has degree of freedom = 5 so, each molecule will require total 5 coordinate variables and 5 momentum variables for their complete description (3-translational, 2-rotational). Hence, each molecule requires 10 phase space dimensions.
Therefore, Total dimension of 10 such molecules in the phase space = $10 \times 10 = 100$.
Hence correct option is (d).

(5 degree of freedom for a rigid diatomic molecule can also be understood by the fact that there are 2 particles each with 3 degree of function but there is one constraint that being rigid, the distance between them is fixed, therefore, total degree of freedom $= 3 + 3 - 1 = 5$).

• Liouville's Theorem

The theorem may be stated in two parts
(1) According to this theorem, the "local" density of the representative points, as viewed by an observer moving with a representative point, stays constant in time. i.e.,

$$\frac{dP}{dt} = \frac{\partial P}{\partial t} + [P, H] = 0$$

P is the probability density. Thus this theorem is also known as the *principle of conservation of the probability density* in phase space.

(2) Any arbitrary element of volume or extension-in-phase in the phase space, bounded by a moving surface and containing a number of phase points does not change with time despite the displacements and distortions. This part represent the principle of conservation of execution in phase space.

• Distinguishable and indistinguishable particles:

Two particles are said to be *distinguishable* when the average distance between them is large compared to their de Broglie wavelength and they don't have overlapping wavepackets.
Distinguishable means they can be described classically (No need of quantum mechanics). *Indistinguishable* particles have overlapped wavepackets. Bosons and fermions are indistinguishable particles. Bosons have integral spin. Fermions have half-integral spin and obeys Pauli's exclusion principle.

• Wave function of two identical particles

According to quantum mechanical theory of identical particles:

For two particles in states n and s represented by wave functions $\phi_n(r_1)$ & $\phi_s(r_2)$ respectively,

We have $\psi_{ns}(r_1, r_2) \equiv$ wave function representing the combined state of the two particles.

Case I. Distinguishable particles (Maxwell-Boltzmann statistics)

$$\psi_{ns}(r_1, r_2) \equiv \phi_n(r_1)\,\phi_s(r_2)$$

Case II. Indistinguishable particles

Case II (A) Fermions (Fermi-dirac statistics)

$$\psi_{ns}(r_1, r_2) \equiv \frac{1}{\sqrt{2}}[\phi_n(r_1)\,\phi_s(r_2) - \phi_n(r_2)\,\phi_s(r_1)]$$

Case II (B) Bosons (Bose-Einstein statistics)

$$\psi_{ns}(r_1, r_2) \equiv \frac{1}{\sqrt{2}}[\phi_n(r_1)\,\phi_s(r_2) + \phi_n(r_2)\,\phi_s(r_1)]$$

- **Density of States**

If we consider the phase space made up of the unit cells where each cell corresponds to a microstate of the given system. Each unit cell has the volume of h^N where h is the Planck's constant and N is the degree of freedom of the particle. For a single particle this volume also can be written as h^D where D is the dimension of the space.

In the case of a single particle in 3-dimentional space, $N=3$; accordingly the number of microstates available would asymptotically be equal to the volume of the allowed region of the phase space divided by h^3. Let $\Sigma(P)$ denote the number of microstates available to a free particle confined to volume V of the physical space, its momentum p being less than or equal to a specified value P. Then

$$\sum(P) \approx \frac{1}{h^3} \int_{p \le P} \ldots \int (d^3q\, d^3p) = \frac{V}{h^3}\frac{4\pi}{3}P^3$$

whence we obtain for the number of microstates with momentum lying between p and $p+dp$

$$g(p)\,dp = \frac{d\sum(p)}{dp}dp \approx \frac{V}{h^3}4\pi p^2 dp$$

Expressed in terms of the particles energy, these expression assume the form

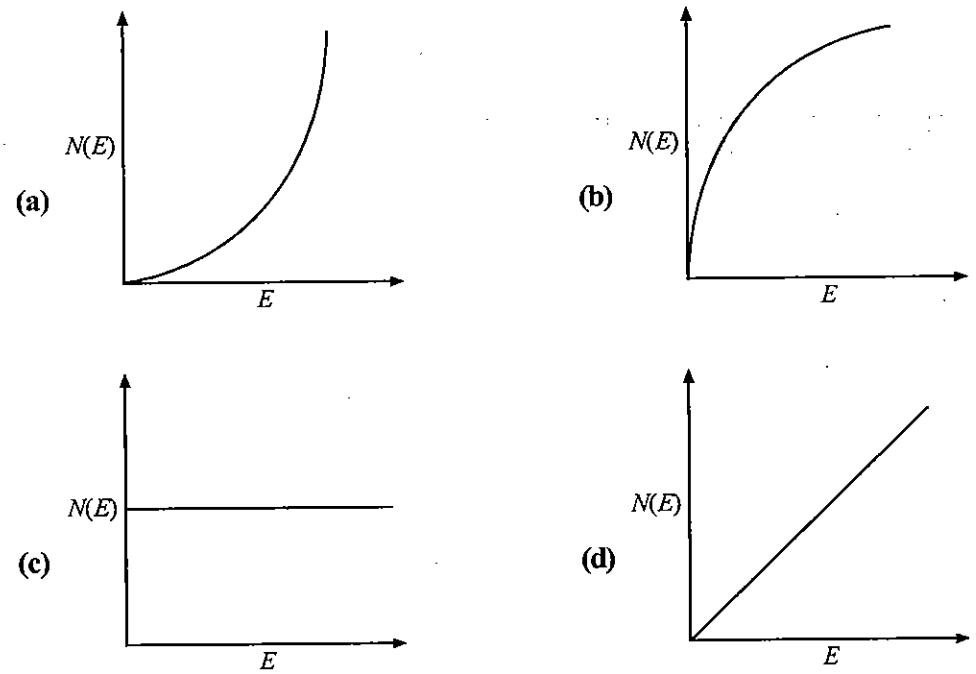
$$\sum(E) \approx \frac{V}{h^3}\frac{4\pi}{3}(2mE)^{3/2} \qquad \left[\because\ p^2 = 2mE\right]$$

and

$$a(\varepsilon)\,d\varepsilon = \frac{d\sum(\varepsilon)}{d\varepsilon}d\varepsilon \approx \frac{V}{h^3}2\pi(2m)^{3/2}\varepsilon^{1/2}d\varepsilon$$

where, $a(\varepsilon)$ is the density of state.

Problem: For a free electron gas in two-dimensions, the variation of the density of states, $N(E)$ as a function of energy E, is best represented by



Soln. For free electron gas in two dimensions, the density of states $N(E)$ has following property $N(E)\,dE \propto d^2p$.

Now, $d^2p = 2\pi p\,dp$

Since, $p^2 = 2mE \Rightarrow 2p\,dp = 2m\,dE$

$\Rightarrow 2p\pi\,dp = 2\pi m\,dE \equiv d^2p$

$\therefore N(E)dE \propto 2\pi m\,dE$

$\Rightarrow N(E)$ is independent of E.

Hence correct option is (c).

Problem: The energy dependence of the density of states for a two dimensional non-relativistic electron gas is given by, $g(E) = CE^n$, where C is constant. The value of n is_____.

Soln. For a two dimensional non-relativistic electron gas the density of states is given by

$$g(E)\,dE = 2\frac{V\,d^2p}{(2\pi\hbar)^2} = 2\frac{V\,2\pi p\,dp}{(2\pi\hbar)^2} = 2\frac{V\,2\pi m\,dE}{(2\pi\hbar)^2}.$$

Thus, $g(E)$ is independent of E

$\Rightarrow g(E) = CE^0$.

Hence the value of n is zero.

Problem: In a classical micro-canonical ensemble for a system of N non-interacting particles, the fundamental volume in phase space which is regarded as "equivalent to one micro-state" is

(a) h^{3N} (b) h^{2N} (c) h^N (d) h

where h is the Planck's constant.

Soln. For one particle, $V = dxdp_x \cdot dydp_y \cdot dzdp_z = h^3$

For N particle, $V = (h^3)^N = h^{3N}$

Hence correct option is (a).

Problem: For an energy state E of a photon gas, the density of states is proportional to

(a) $\sqrt{E}$ (b) E (c) $E^{3/2}$ (d) E^2

Soln. Density of states is defined as

$$\mathcal{D}(E) = \frac{4\pi g p^2}{(2\pi\hbar)^3}\left(\frac{dp}{dE}\right)$$

where p = momentum of the particle.

For photons we have $E = pc \Rightarrow p^2 = \frac{E^2}{c^2}$ and $\frac{dp}{dE} = \frac{1}{c}$.

$$\therefore \mathcal{D}(E) = \frac{4\pi g E^2}{(2\pi\hbar c)^3} \Rightarrow \mathcal{D}(E) \propto E^2$$

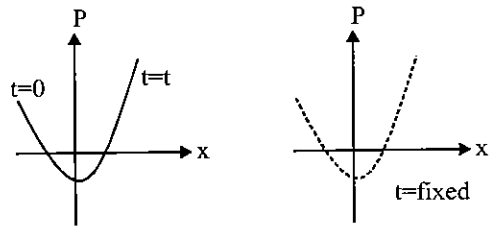
Hence correct option is (d).

Ensembles in Statistical Physics

The description of any system in statistical physics is done by considering ensembles. Once we know our ensemble (collection of systems etc.), we can quickly apply the laws of statistical mechanics to it and understand the physics thereof.

Part of phase line constructed due to the motion of phase point with time. Each phase point on the line corresponds to different time co-ordinates.

Gibbs replace this time dependent picture by a static picture (time fix) in which the entire phase line exists at one time. Then each phase point represents a seperate system that are macroscopically identical but microscopically different to the system of interest. These systems are non-interacting independent system. All members are identical in features like N,V,E. (macrostate) but differing position and momenta co-ordinates of individual molecules (microscopically)



A collection of large no. of independent systems which are macroscopically identical but microscopically different is called *ensemble*.

The concept of ensemble helps in understanding the actual system more completely. It represents at one time the microstate of actual system which would occur in the course of time. We study the statistical behaviour of the ensemble by the knowledge of the behaviour of the ensemble. We can predict the probable behaviour of the system under consideration.

The various types of ensembles are :

1. Microcanonical ensemble

It is the ensemble in which all element have same macrostate represented by same no. of particle N, same volume V and same energy E i.e. macrostate is specified by (N,V, E) for all elements (systems). All elements of microcanonical ensemble are separated by impenetrable, rigid and non-conducting walls such that values of (N, V, E) for a particular system are not affected by the presence of other system i.e. all systems are isolated to each other.

2. Canonical ensemble

It is the ensemble in which all elements will have same macrostate represent by same N,V, T for all elements. The elements of a canonical ensemble are separated from each other by impeneterable, rigid and conducting walls such that the values of N, V, T for a particular system are not affected by others. In canonical ensemble each element is in thermal contact (equilibrium) with heat reservoir or with all other elements of the ensemble at temperature T. In this ensemble elements can exchange energy but not particle.

3. Grand canonical ensemble

It is the ensemble in which all elements will have same macrostate represent by same μ, V, T for all elements. The elements of a grand canonical ensemble are separated from each other by penetrable, rigid and conducting walls such that the values of μ, V, T for a particular system aren't affected by others. In this ensemble the elements are in contact with particle energy reservoir. The elements can exchange energy as well as particle.

Microcanonical Ensemble

For microcanonical ensemble, energy remains constant (systems are isolated)

- **Contact between Statistics and Thermodynamics**

The actual number of all possible microstates will, of course, be a function of N, V and E and may be denoted by the symbol $\Omega(N, V, E)$. Then the entropy of the system is defined as

$$S = k_B \ell n \Omega$$

where k_B is Boltzmann's constant. As it stands, this formula determines the absolute value of the entropy of a given physical system in terms of the total number of microstates (Ω) accessible to it confirmly with the given macrostate. The zero of entropy then corresponds to the special state for which only one microstate ($\Omega = 1$) is accessible the so called *unique configuration*; the statistical approach thus provides a theoretical basis for the third law of thermodynamics.

Further contact is established with the help of laws of thermodynamics as

$$dQ = dE + dW$$

$$\Rightarrow \quad TdS = dE + PdV - \mu dN \qquad ...(1)$$

where μ is chemical potential and N is total number of particles. From equation (1),

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}; \left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{P}{T}; \left(\frac{\partial S}{\partial N}\right)_{V,E} = -\frac{\mu}{T}$$

Also we can write using the well known relationship in partial differential calculus namely that if three variables x, y and z are mutually related then

$$\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$P = \left(\frac{\partial S}{\partial V}\right)_{N,E} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = -\left(\frac{\partial E}{\partial V}\right)_{N,S}$$

and $$\mu = -\left(\frac{\partial S}{\partial N}\right)_{V,E} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial E}{\partial N}\right)_{V,S}$$

while $$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$$

The rest of thermodynamics follows straight forwardly. For instance the Helmholtz free energy F, the Gibbs free energy G and the enthalpy H are given by

$$F = E - TS$$

$$G = F + PV = E - TS + PV = \mu N \text{ and } H = E + PV = G + TS$$

The specific heat at constant volume C_V and the one at constant pressure C_P, would be given by

$$C_V = T \cdot \left(\frac{\partial S}{\partial T}\right)_{N,V} = \left(\frac{\partial E}{\partial T}\right)_{N,V} \text{ and}$$

$$C_P = T \cdot \left(\frac{\partial S}{\partial T}\right)_{N,P} = \left(\frac{\partial (E + PV)}{\partial T}\right)_{N,P} = \left(\frac{\partial H}{\partial T}\right)_{N,P}$$

Problem: The chemical potential of an ideal Bose gas at any temperature is : **[JAM-2008]**

(a) Necessarily negative (b) Either zero or negative
(c) Necessarily positive (d) Either zero or positive

Soln. The chemical potential μ for an ideal Bose gas is either zero or negative.
Correct option is (b)

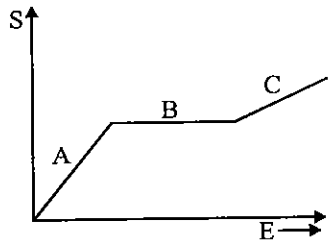
Problem: The entropy of a system, S, is related to the accessible phase space volume Γ by $S = k_B \ell n \Gamma(E, N, V)$ where E, N and V are the energy, number of particles and volume respectively. From this one can conclude that

(a) does not change during evolution to equilibrium
(b) Oscillates during evolution to equilibrium
(c) Is a maximum in equilibrium
(d) Is a minimum in equilibrium

Soln. In the micrononical ensemble, the phase volume is maximized to obtain the characteristic thermodynamics quantity which is entropy.

Correct option is (c)

Problem: The entropy S of a thermodynamic system as a function of energy E is given by the following graph



The temperatures of the phases A, B and C, denoted by T_A, T_B and T_C, respectively, satisfy the following inequalities:

(a) $T_C > T_B > T_A$ (b) $T_A > T_C > T_B$ (c) $T_B > T_C > T_A$ (d) $T_B > T_A > T_C$

Soln. $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)$

$\left(\frac{\partial S}{\partial E}\right)_A > \left(\frac{\partial S}{\partial E}\right)_C > \left(\frac{\partial S}{\partial E}\right)_B$

$\Rightarrow T_B > T_C > T_A$

Correct answer is (c)

Problem: The internal energy E of a system is given by $E = \frac{bS^3}{VN}$, where b is a constant and other symbols have their usual meaning . The temperature of this system is equal to

(a) $\frac{bS^2}{VN}$ (b) $\frac{3bS^2}{VN}$ (c) $\frac{bS^3}{V^3N}$ (d) $\left(\frac{S}{N}\right)^2$

Soln. $E = \frac{bS^3}{VN}$

$\because \quad dQ = TdS = dE + PdV - \mu dN$

$\Rightarrow \quad T = \left(\frac{\partial E}{\partial S}\right)_{N,V} = \frac{3bS^2}{NV}$

Correct answer is (b)

Problem: A paramagnetic system consisting of N spin-half particles, is placed in an external magnetic field. It is found that $N/2$ spins are aligned parallel and the remaining $N/2$ spins are aligned antiparallel to the magnetic field. The statistical entropy of the system is,

(a) $2Nk_B \ell n\, 2$ (b) $\frac{N}{2} k_B\, \ell n\, 2$ (c) $\frac{3N}{2} k_B\, \ell n\, 2$ (d) $Nk_B\, \ell n\, 2$

Soln. For spin- 1/2 system, number of microstates under equilibrium condition (as the given spin configuration is analogous to equilibrium spin configuration)

$\Omega = (2s+1)^N = 2^N$

Therefore, Entropy $S = k_B\ \ell n\ \Omega = k_B\ \ell n\ 2^N = Nk_B\ \ell n\ 2$

Hence correct option is (d).

Problem: The total energy, E of an ideal non-relativistic Fermi gas in three dimensions is given by $E \propto \frac{N^{5/3}}{V^{2/3}}$ where N is the number of particles and V is the volume of the gas. Identify the correct equation of state (P being the pressure),

(a) $PV = \frac{1}{3}E$ (b) $PV = \frac{2}{3}E$ (c) $PV = E$ (d) $PV = \frac{5}{3}E$

Soln. Let, $E = \frac{K}{V^{2/3}}$ ...(i)

Now, $P = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = -\frac{\partial}{\partial V}\left(\frac{K}{V^{2/3}}\right) = \frac{2}{3}KV^{-5/3} = \frac{2}{3}\frac{K}{V^{5/3}}$ or $P = \frac{2K}{3V \times V^{2/3}}$

$PV = \frac{2}{3}\frac{K}{V^{2/3}} = \frac{2}{3}E$ [Using equation (i)]

Hence correct option is (d).

Problem: The entropy of a gas containing N particles enclosed in a volume V is given by $S = Nk_B\ \ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right)$, where E is the total energy, a is a constant and k_B is the Boltzmann constant. The chemical potential μ of the system at a temperature T is given by

(a) $\mu = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - \frac{5}{2}\right]$ (b) $\mu = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - \frac{3}{2}\right]$

(c) $\mu = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{3/2}}\right) - \frac{5}{2}\right]$ (d) $\mu = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{3/2}}\right) - \frac{3}{2}\right]$

Soln. $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{V,E} = -T\,k_B\ \ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - T\,k_BN \cdot \frac{N^{5/2}}{\cancel{aVE^{3/2}}} \cdot \cancel{aVE^{3/2}}\left(-\frac{5}{2}N^{-7/2}\right)$

$= -T\,k_B\ \ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) + \frac{5}{2}k_BT = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - \frac{5}{2}\right]$

Hence correct option is (a).

Problem: Consider a linear collection of N independent spin 1/2 particles, each at a fixed location. The entropy of this system is (k is the Boltzmann constant)

(a) Zero (b) Nk (c) ½ Nk (d) $Nk\ ln(2)$

Soln. The number of microstates for a particle with spin $S = 2S + 1$.

Therefore, total number of accessible microstates for N independent spins $= (2S + 1)^N = \Omega$.

Now, entropy $\equiv k_B\ \ell n\ \Omega = k_B\ \ell n\left[(2S+1)^N\right]$

Putting $S = 1/2$, we have

Entropy $= k_B\ \ell n\left[(1+1)^N\right] = Nk_B\ \ell n\ 2$

Hence correct option is (d).

Problem: The total number of accessible states of N non-interacting particles of spin 1/2 is

(a) 2^N (b) N^2 (c) $2^{N/2}$ (d) N

Soln. The total number of accessible states for N non-interacting spin(S) particles $= (2S+1)^N$.

So, for spin $S = \frac{1}{2}$ particles, number of states $= \left(2\times\frac{1}{2}+1\right)^N = 2^N$

Hence, the correct option is (a).

The Canonical Ensemble

A system in contact with a heat reservoir of infinite heat capacity or in thermal equilibrium at temperature T and having N particles confined to a volume V is considered as canonical ensemble.

The whole thermodynamics of the canonical ensemble is understood in terms of partition function.

Partition Function

Let us consider an assembly of ideal gas molecules obeying quantum statistics. Let the distribution of gas molecules be such that n_i molecules occupy the ith state with energy ε_i and degeneracy (i.e., the number of energy levels with the same energy) g_i. Then from Maxwell-Boltzmann distribution law, we have

$$n_i = g_i e^{-\alpha} e^{-\varepsilon_i/k_BT}$$

Let us substitute $e^{-\alpha} = A$. Then $n_i = g_i A e^{-\varepsilon_i/k_BT}$

If the total number of gas molecules in the assembly is N, then

$$N = \sum_i n_i = \sum_i g_i A e^{-\varepsilon_i/k_BT}$$

$$= A\sum_i g_i e^{-\varepsilon_i/k_BT} \qquad ...(1)$$

The term $A(= e^{-\alpha})$ has been taken out of the summation sign because α is a constant.

From equation (1), we get

$$\frac{N}{A} = \sum_i g_i e^{-\varepsilon_i/k_BT} = Z \text{ (say)} \qquad ...(2)$$

The quantity Z is called the Boltzmann partition function or simply the partition function. Therefore, the quantity Z indicates how the gas molecules of an assembly are distributed or partitioned among the various energy levels.

If the energy of the ith level is ε_i then keeping in mind that the weight of an individual level is unity equation (2) can be written as

$$Z = \sum_i e^{-\varepsilon_i/k_BT}$$

And if particle obeys classical statistics then $Z = \int g(\varepsilon)\cdot e^{-\varepsilon/k_BT} d\varepsilon$

Partition Function and Thermodynamic Quantities

If $Z_1(V,T)$ is the partition function of a single particle then the partition function of the system having N independent particles is given by $Z_N(V,T)=[Z_1(V,T)]^N$ if particles are distinguishable and $Z_N(V,T)=\frac{[Z_1(V,T)]^N}{N!}$ if particles are indistinguishable.

The Helmholtz free energy of the system is given by $F=-k_BT\cdot \ell n\{Z_N(V,T)\}$.

As we know $F=U-TS$

or $dF=dU-TdS-SdT$

or $dF=-SdT-PdV+\mu dN \qquad \{\because\ dU=TdS-PdV+\mu dN\}$

So $S=-\left(\frac{\partial F}{\partial T}\right)_{N,V}$; $P=-\left(\frac{\partial F}{\partial V}\right)_{N,T}$ and $\mu=\left(\frac{\partial F}{\partial N}\right)_{V,T}$

Also $U=F+TS=F-T\left(\frac{\partial F}{\partial T}\right)_{N,V}=-T^2\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_{N,V}=\left[\frac{\partial (F/T)}{\partial (1/T)}\right]_{N,V}$

$C_V=\left(\frac{\partial U}{\partial T}\right)_{N,V}=-T\left(\frac{\partial^2 F}{\partial T^2}\right)_{N,V}$

and the Gibbs free energy is $G=F+PV=F-V\left(\frac{\partial F}{\partial T}\right)_{N,T}=N\left(\frac{\partial F}{\partial N}\right)_{V,T}=N\mu$

Hence all thermodynamics is derived from partition function $Z=\sum g_i\cdot e^{-\varepsilon_i/kT}$.

Problem: The free energy of a gas N particled in a volume V and at a temperature T is $F=NK_BT\ln\left[a_0V(k_BT)^{5/2}/N\right]$, where a_0 is a constant and k_B denotes the Boltzmann constant. The internal energy of gas is

(a) $\frac{3}{2}Nk_BT$ (b) $\frac{5}{2}Nk_BT$

(c) $Nk_BT\ln\left[a_0V(k_BT)^{5/2}/N\right]-\frac{3}{2}Nk_BT$ (d) $Nk_BT\ln\left[a_0V/(k_BT)^{5/2}\right]$

Soln. The Free energy, $F=Nk_BT\,\ell n\left[a_oV(k_BT)^{5/2}/N\right]=k_BT\,\ell n\left[a_oV(k_BT)^{5/2}/N\right]^N$

As $F=-k_BT\,\ell n\,Z$, we have

$\ell n\,Z=-\ell n\left[a_oV(k_BT)^{5/2}/N\right]^N$

$\Rightarrow U=-\frac{\partial}{\partial\beta}\ell n\,Z=k_BT^2\frac{\partial}{\partial T}\ell n\,Z \qquad \left[\because \beta=\frac{1}{k_BT}\Rightarrow \partial\beta=\frac{-1}{k_BT^2}\partial T\right]$

$=k_BT^2\frac{\partial}{\partial T}\left[-\ell n\left\{a_oV(k_BT)^{5/2}/N\right\}^N\right]=k_BT^2\frac{\partial}{\partial T}\left[-\ell n\,T^{\frac{5N}{2}}-\ell n\left(\frac{a_oVk_B^{5/2}}{N}\right)^N\right]$

$=-\frac{5N}{2}k_BT^2\times\frac{1}{T}=-\frac{5}{2}N\,k_BT$ [Extra -ve sign is due to the wrong sign in the given question]

Correct answer is (b).

Problem: The free energy for a photon gas is given by $F = -\left(\frac{a}{3}\right)VT^4$, where a is a constant. The entropy S and the pressure P of the photon gas are

(a) $S = \frac{4}{3}aVT^3, P = \frac{a}{3}T^4$ (b) $S = \frac{1}{3}aVT^4, P = \frac{4a}{3}T^3$

(c) $S = \frac{4}{3}aVT^4, P = \frac{a}{3}T^3$ (d) $S = \frac{1}{3}aVT^3, P = \frac{4a}{3}T^4$

Soln. $F = -\frac{a}{3}VT^{+4}$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{a}{3}T^4$$

$$S = \left(\frac{\partial F}{\partial T}\right)_V = \frac{4}{3}aVT^3$$

Hence correct option is (a).

Problem: The partition function of a single gas molecule is Z_α. The partition function of N such non-interacting gas molecules is then given by

(a) $\frac{(Z_\alpha)^N}{N!}$ (b) $(Z_\alpha)^N$ (c) $N(Z_\alpha)$ (d) $\frac{(Z_\alpha)^N}{N}$

Soln. Gas molecules $\Rightarrow$ distinguishable (classical particles). If Z_α = partition function for single particle, then for N distinguishable particles the partition function = $(Z_\alpha)^N$. On the other hand, for N non-distinguishable particles, the partition function = $\frac{(Z_\alpha)^N}{N!}$.

Hence, the correct option is (b).

Problem: The free energy of a photon gas enclosed in a volume V is given by $F = -\frac{1}{3}aVT^{-4}$, where a is a constant and T is the temperature of the gas. The chemical potential of the photon gas is

(a) zero (b) $\frac{4}{3}aVT^3$ (c) $\frac{1}{3}aT^{-4}$ (d) aVT^{-4}

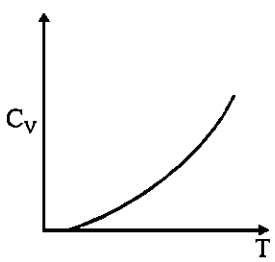
Soln. $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$; for this case $F = -\frac{1}{3}aVT^{-4}$ which is independent of N. Therefore, $\mu = 0$. Anyway, for photon gas (in equilibrium) $\mu = 0$.

Hence, the correct option is (a).

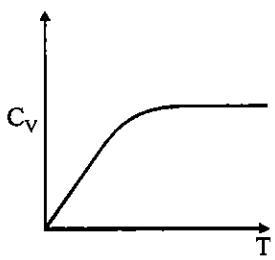
Problem: The partition function for a gas of photons is given by $\ell n\, Z = \frac{\pi^2}{45}\frac{V(k_BT)^3}{\hbar^3c^3}$.

The specific heat of the photon gas veries with temperature as

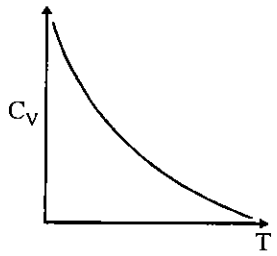
(a)



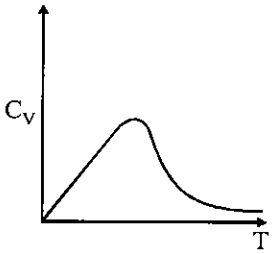
(b)



(c)



(d)



Soln. Here, $\log Z = \frac{\pi^2}{45} V \frac{(k_B T)^3}{\hbar^3 c^3}$

Putting $k_B T = \frac{1}{\beta}$, we get $\log Z = \frac{\pi^2}{45} \frac{V}{\hbar^3 c^3} \frac{1}{\beta^3}$

$$U = -\frac{\partial}{\partial \beta} \log Z = -\frac{\pi^2}{45} \frac{V}{\hbar^3 c^3} \frac{(-3)}{\beta^4} = \frac{\pi^2}{15} \frac{V}{\hbar^3 c^3} (k_B T)^4 \quad \because \beta = \frac{1}{k_B T}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{4\pi^2}{15} \frac{V k_B^4}{\hbar^3 c^3} T^3 \Rightarrow C_V \propto T^3$$

Hence correct option is (b).

Problem: Common Data for next two problems :

Consider a two levels quantum system with energies $\varepsilon_1 = 0,\ \varepsilon_2 = \varepsilon$.

(i) The Helmholtz free energy of the system is given by

(a) $-k_B T\ \ell n\ (1 + e^{-\varepsilon/k_B T})$

(b) $k_B T\ \ell n\ (1 + e^{-\varepsilon/k_B T})$

(c) $\frac{3}{2} k_B T$

(d) $\varepsilon - k_B T$

Soln. $F = -k_B T \log\left[e^{-\varepsilon_1/k_B T} + e^{-\varepsilon_2/k_B T}\right]$ $\left[\because\ \varepsilon_1 = 0,\ \varepsilon_2 = \varepsilon\right]$

$$F = -k_B T \log\left[1 + e^{-\varepsilon/k_B T}\right]$$

Hence correct option is (a).

CAREER ENDEAVOUR

(ii) The specific heat of the system is given by

(a) $\frac{\varepsilon}{k_B T} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})^2}$

(b) $\frac{\varepsilon^2}{k_B T^2} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})}$

(c) $-\frac{\varepsilon^2\, e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})^2}$

(d) $\frac{\varepsilon^2}{k_B T^2} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})^2}$

Soln. $\frac{\partial F}{\partial T} = \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})} \times \left(\frac{-\varepsilon}{k_B T^2}\right) \times (-k_B T) = \frac{\varepsilon}{T} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})}$

$$C_V = \frac{\varepsilon}{k_B T} \times \frac{\partial F}{\partial T} = \frac{\varepsilon^2}{k_B T^2} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})}$$

Hence correct option is (b).

Statistical Average of a Physical Quantity

Statistical average of a physical quantity "f" is given by $\langle f \rangle = \dfrac{\sum_i f_i g_i \cdot e^{-\varepsilon_i / k_B T}}{\sum_i g_i \cdot e^{-\varepsilon_i / k_B T}}$

Statistical average of energy and relative root mean square fluctuation in energy:

$$U = \langle E \rangle = \frac{\sum_i \varepsilon_i \cdot g_i \, e^{-\beta \varepsilon_i}}{\sum_i g_i \cdot e^{-\beta \varepsilon_i}}; \quad \beta = \frac{1}{k_B T}$$

Differentiate it with respect to parameter β, holding the energy values ε_i constant, we obtain

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_i \varepsilon_i^2 \cdot g_i \, e^{-\beta \varepsilon_i}}{\sum_i g_i \cdot e^{-\beta \varepsilon_i}} + \left[\frac{\sum_i \varepsilon_i \, g_i \, e^{-\beta \varepsilon_i}}{\sum_i g_i \cdot e^{-\beta \varepsilon_i}} \right]^2$$

whence if follow that $\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = -\dfrac{\partial U}{\partial \beta} = kT^2 \left(\dfrac{\partial U}{\partial T} \right) = kT^2 C_V$

and the relative root-mean-square fluctuation in E

$$\frac{\sqrt{[\langle (\Delta E)^2 \rangle]}}{\langle E \rangle} = \frac{\sqrt{kT^2 C_V}}{U}$$

Problem: Consider a system of two non-interacting classical particles which can occupy any of the three energy levels with energy values $E = 0$, e and 2e having degeneracies $g(E) = 1, 2$ and 4 respectively. The mean energy of the system is

(a) $\varepsilon \left[\dfrac{4 \exp\left(\frac{-\varepsilon}{k_B T}\right) + 8 \exp\left(\frac{-2\varepsilon}{k_B T}\right)}{1 + 2 \exp\left(\frac{-\varepsilon}{k_B T}\right) + 4 \exp\left(\frac{-2\varepsilon}{k_B T}\right)} \right]$ (b) $\varepsilon \left[\dfrac{2 \exp\left(\frac{-\varepsilon}{k_B T}\right) + 8 \exp\left(\frac{-2\varepsilon}{k_B T}\right)}{1 + 2 \exp\left(\frac{-\varepsilon}{k_B T}\right) + 4 \exp\left(\frac{-2\varepsilon}{k_B T}\right)} \right]$

(c) $\varepsilon \left[\dfrac{2 \exp\left(\frac{-\varepsilon}{k_B T}\right) + 4 \exp\left(\frac{-2\varepsilon}{k_B T}\right)}{1 + 2 \exp\left(\frac{-\varepsilon}{k_B T}\right) + 4 \exp\left(\frac{-2\varepsilon}{k_B T}\right)} \right]^2$ (d) $\varepsilon \left[\dfrac{\exp\left(\frac{-\varepsilon}{k_B T}\right) + 2 \exp\left(\frac{-2\varepsilon}{k_B T}\right)}{1 + \exp\left(\frac{-\varepsilon}{k_B T}\right) + \exp\left(\frac{-2\varepsilon}{k_B T}\right)} \right]$

Soln. Total energy due to a particular level = occupancy of the level × energy.

$$\therefore \quad E_1 = 0 \cdot \exp\left[-\frac{0}{k_B T} \right]$$

$$E_2 = \varepsilon \cdot g(E) \cdot \exp\left[-\frac{\varepsilon}{k_B T} \right] = 2\varepsilon \exp\left[-\frac{\varepsilon}{k_B T} \right]$$

Similarly, $E_3 = 2\varepsilon \cdot 4 \exp\left[-\dfrac{2\varepsilon}{k_B T} \right]$

$$\text{Also, mean energy} = \frac{\sum_i E_i}{\text{total occupancy}} = \frac{E_1 + E_2 + E_3}{\sum_i g_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)}$$

$$= \frac{0 + 2\varepsilon \exp\left(-\frac{\varepsilon}{k_B T}\right) + 8\varepsilon \exp\left(-\frac{2\varepsilon}{k_B T}\right)}{\exp\left(-\frac{0}{k_B T}\right) + 2\exp\left(-\frac{\varepsilon}{k_B T}\right) + 4\exp\left(-\frac{2\varepsilon}{k_B T}\right)} = \varepsilon\left[\frac{2\exp\left(-\frac{\varepsilon}{k_B T}\right) + 4\exp\left(-\frac{2\varepsilon}{k_B T}\right)}{1 + 2\exp\left(-\frac{\varepsilon}{k_B T}\right) + 4\exp\left(-\frac{2\varepsilon}{k_B T}\right)}\right]$$

Hence correct option is (b).

Problem: A system has two energy levels with energies ε and 2ε. The lower level is 4-fold degenerate while the upper level is doubly degenerate. If there are N non-interacting classical particles in the system, which is in thermodynamic equilibrium at a temperature T, the fraction of particles in the upper level is:

(a) $\frac{1}{1+e^{-\varepsilon/k_B T}}$ (b) $\frac{1}{1+2e^{\varepsilon/k_B T}}$ (c) $\frac{1}{2e^{\varepsilon/k_B T}+4e^{2\varepsilon/k_B T}}$ (d) $\frac{1}{2e^{\varepsilon/k_B T}-4e^{2\varepsilon/k_B T}}$

Soln. $E_L = E,\ E_U = 2E$

$g_L = 4,\ g_U = 2$

$$N(E_i) \propto g_i \exp\left[-\frac{E_i}{k_B T}\right]$$

$$\therefore\ N(E_L) = C \times g_L \exp\left[-\frac{E_L}{k_B T}\right]$$

$$\text{Similarly, } N(E_U) = C \times g_U \exp\left[-\frac{E_U}{k_B T}\right]$$

$$\text{The fraction of particles in upper level} = \frac{N(E_U)}{N(E_U) + N(E_L)}$$

$$= \frac{2 \cdot \exp\left[-\frac{2E}{k_B T}\right]}{4\exp\left[-\frac{E}{k_B T}\right] + 2\exp\left[-\frac{2E}{k_B T}\right]} = \frac{1}{1 + 2\exp\left[\frac{E}{k_B T}\right]}$$

Hence correct option is (b).

Problem: N distinguishable particles are distributed among three states having energies 0, $k_B T$ and $2k_B T$ respectively. If the total equilibrium energy of the system is 151.23 $k_B T$, the number of particles of the system is about

(a) 152 (b) 264 (c) 356 (d) 635 **[D.U.-2016]**

Soln. The average energy is

$$\langle E \rangle = \frac{N\left[0\, e^{-0/k_B T} + k_B T\, e^{-k_B T/k_B T} + 2k_B T\, e^{-2k_B T/k_B T}\right]}{e^{-0/k_B T} + e^{-k_B T/k_B T} + e^{-2k_B T/k_B T}} = 151.23\, k_B T$$

$$\Rightarrow \frac{N\left[k_B T\left(e^{-1}+2e^{-2}\right)\right]}{1+e^{-1}+e^{-2}} = 151.23\, k_B T$$

$$\Rightarrow N = \left(\frac{1+e^{-1}+e^{-2}}{e^{-1}+2e^{-2}}\right) 151.23 = 356.01$$

Correct option is (c)

Problem: Consider a Maxwell-Boltzmann system with two states of energies E and 2E. If each state is two-fold degenerate, then the partition function would be (in terms of E, k and T, where k is the Boltzmann constant and T is the absolute temperature):

(a) $z = 2e^{-3E/kT}$ (b) $z = e^{-E/kT}\left[1+2e^{-E/kT}\right]$

(c) $z = 2e^{-E/kT}\left[1+e^{-2E/kT}\right]$ (d) $z = 2e^{-E/kT}\left[1+e^{-E/kT}\right]$

Soln. The partition function is

$$z = \sum_i g_i\, e^{-E_i/kT}$$

where g_i is the degeneracy of the E_i the state.

So, $z = 2e^{-E/kT} + 2e^{-2E/kT} = 2e^{-E/kT}\left[1+e^{-E/kT}\right]$

Correct option is (d)

Problem: A particle in thermal equilibrium has only 3 possible states with energies $-\varepsilon$, 0, ε. If the system is maintained at a temperature $T >> \frac{\varepsilon}{k_B}$, then the average energy of the particle can be approximated to,

(a) $\frac{2\varepsilon^2}{2k_B T}$ (b) $-\frac{2\varepsilon^2}{3k_B T}$ (c) $\frac{\varepsilon^2}{k_B T}$ (d) 0 **[JEST-2015]**

Soln. The average energy is

$$\langle E\rangle = \frac{-\varepsilon e^{\varepsilon/k_B T} + 0\, e^{-0/k_B T} + \varepsilon e^{-\varepsilon/k_B T}}{e^{+\varepsilon/k_B T} + e^{-0/k_B T} + e^{-\varepsilon/k_B T}}$$

$$= \frac{\varepsilon\left(e^{-\varepsilon/k_B T} - e^{\varepsilon/k_B T}\right)}{e^{-\varepsilon/k_B T} + 1 + e^{\varepsilon/k_B T}} = \frac{\varepsilon\left(1-e^{2\varepsilon/k_B T}\right)}{1+e^{\varepsilon/k_B T}+e^{2\varepsilon/k_B T}}$$

for $T >> \frac{\varepsilon}{k_B}$ or $\varepsilon << k_B T$, we have

$$\langle E\rangle = \frac{\varepsilon\left[1-\left(1+2\varepsilon/k_B T\right)\right]}{1+1+\varepsilon/k_B T+1+2\varepsilon/k_B T} = \frac{-2\varepsilon^2/k_B T}{3+3\varepsilon/k_B T}$$

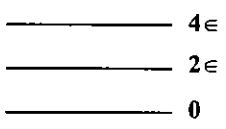
$$\Rightarrow \langle E\rangle = -\frac{2\varepsilon^2}{3k_B T} \qquad \left[\because\ 1+\frac{\varepsilon}{k_B T} \approx 1 \text{ for } \frac{\varepsilon}{k_B T} << 1\right]$$

Correct option is (b)

Problem: A gas of N non-interacting particles is in thermal equilibrium at temperature T. Each particle can be in any of the possible non-degenerate states of energy 0, 2ε and 4ε. The average energy per particle of the gas, when $\beta\varepsilon \ll 1$, is:

(a) 2ε (b) 3ε (c) $2\varepsilon/3$ (d) ε

Soln.



$$\langle E\rangle = \frac{0.e^{-0/k_BT} + 2\varepsilon\, e^{-2\varepsilon/k_BT} + 4\varepsilon\, e^{-4\varepsilon/k_BT}}{e^{-0/k_BT} + e^{-2\varepsilon/k_BT} + e^{-4\varepsilon/k_BT}} = \frac{2\in\left[e^{-2\varepsilon/k_BT} + 2e^{-4\varepsilon/k_BT}\right]}{1 + e^{-2\varepsilon/k_BT} + e^{-4\varepsilon/k_BT}}$$

Since, $\beta\varepsilon << 1$, $\frac{\varepsilon}{k_BT} << 1 \Rightarrow$ we retain only the first term of exponentials.

Therefore, $\langle E\rangle = \frac{2\varepsilon(1+2)}{(1+1+1)} = 2\varepsilon$

Correct answer is (a)

Harmonic Oscillator System

For a system of N oscillators, each of mass m and angular frequency ω

(i) In classical mechanics, the Hamiltonian of an oscillator is $H = p^2/2m + m\omega^2 q^2/2$. Thus, the classical partition function in 1-D is

$$Z_1 = \frac{1}{h}\int e^{-E/k_BT}\,dq\,dp = \frac{1}{h}\int_{-\infty}^{\infty} e^{-p^2/2mk_BT}\,dp \int_{-\infty}^{\infty} e^{-m\omega^2 q^2/2k_BT}\,dq = \frac{1}{h}\sqrt{2\pi mk_BT}\,\sqrt{\frac{2\pi k_BT}{m\omega^2}} = \frac{2\pi k_BT}{h\omega}$$

(ii) In quantum mechanics, the energy of an oscillator is $E_n = (n + 1/2)\hbar\omega$. Thus, the quantum mechanical partition function is

$$Z_1 = \sum_n e^{-E_n/k_BT} = \sum_{n=0}^{\infty} e^{-(n+1/2)\hbar\omega/k_BT} = e^{-\hbar\omega/2k_BT}\sum_{n=0}^{\infty}(e^{-\hbar\omega/k_BT})^n$$

$$= \frac{e^{-\hbar\omega/2k_BT}}{1 - e^{-\hbar\omega/k_BT}} = \frac{1}{e^{\hbar\omega/2k_BT} - e^{-\hbar\omega/2k_BT}} = \frac{1}{2\sinh(\hbar\omega/2k_BT)}$$

It is obvious that when $(\hbar\omega/k_BT) \to 0$ the case (ii) converges into (i). Therefore, here in after, we shall consider only the case (ii).

Since the partition function Z_N of a system of N independent partitions is equal to the product of the partition function Z_1 of individual particle, we have

$$Z_N = Z_1^N = \left[2\sinh\frac{\hbar\omega}{2k_BT}\right]^{-N}$$

Using $\beta = 1/k_BT$, the internal energy U of the system is

$$U = -\frac{\partial}{\partial\beta}\ell n\, Z_N = N\frac{\partial}{\partial\beta}\ell n\left[\sinh\frac{\beta\hbar\omega}{2}\right] = N\left[\frac{\hbar\omega}{2}\right]\coth\frac{\hbar\omega}{2k_BT} = N\left[\frac{\hbar\omega}{2} + \frac{1}{e^{\hbar\omega/k_BT} - 1}\right]$$

Specific heat at constant volume C_V is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,\omega} = Nk\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2}\left[\frac{\hbar\omega}{kT}\right]^2 = N\left[\frac{\hbar\omega}{2} + kT\,\ell n\,(1 - e^{-\hbar\omega/kT})\right]$$

The entropy S is

$$S = \frac{U-F}{T} = Nk\left[\frac{\hbar\omega}{2kT}\coth\frac{\hbar\omega}{2kT} - \ell n\left(2\sinh\frac{\hbar\omega}{2kT}\right)\right]$$

Problem: If the partition function of a harmonic oscillator with frequency ω at a temperature T is $\frac{k_B T}{\hbar\omega}$, then the free energy of N such independent oscillators is:

(a) $\frac{3}{2}Nk_BT$ (b) $k_BT\ln\frac{\hbar\omega}{k_BT}$ (c) $Nk_BT\ln\frac{\hbar\omega}{k_BT}$ (d) $Nk_BT\ln\frac{\hbar\omega}{2k_BT}$

Soln. The Helmholtz' free energy of N independent harmonic oscillator in terms of partition function Z is

$$F = -Nk_BT\ \ell n\ Z$$

In question, $Z = \frac{k_BT}{\hbar\omega}$

So, $F = -Nk_BT\ \ell n\ Z = Nk_BT\ \ell n\frac{1}{Z} = Nk_BT\ \ell n\frac{\hbar\omega}{k_BT}$

Hence correct option is (c).

Problem: A system is in thermal equilibrium has energies 0 and E. Calculate thermodynamic properties of the system.

Soln. Let T be the temperature of the system. The partition function Z of the system is

$$Z = e^{0/k_BT} + e^{-E/k_BT} = 1 + e^{-E/k_BT}$$

(i) Free energy F of the system is

$$F = -k_BT\ \ell n\ Z = -k_BT\ \ell n\left[1+e^{-E/k_BT}\right]$$

(ii) Entropy S of the system is $S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = k\ \ell n\left[1+e^{-E/k_BT}\right] + \frac{E}{T^2}\frac{1}{e^{E/k_BT}+1}$

(iii) Internal energy U is

$$U = F + ST$$

$$= -k_BT\ \ell n\left[1+e^{-E/k_BT}\right] + k_BT\ \ell n\left[1+e^{-E/k_BT}\right] + \frac{E}{e^{E/k_BT}+1}$$

$$= \frac{E}{e^{E/k_BT}+1} \qquad ...(1)$$

(iv) Specific heat at constant volume C_V is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = k_B\left(\frac{E}{k_BT}\right)^2\frac{e^{E/k_BT}}{\left(e^{E/k_BT}+1\right)^2} \qquad ...(2)$$

(a) At a low temperature $(E/k_BT) \gg 1$, and equation (2) reduces to

$$C_V = k_B\left(\frac{E}{k_BT}\right)^2 e^{-E/k_BT}$$

Since with the decreases of T, the function e^{-E/k_BT} reduces much faster than the increases of the function $(E/k_BT)^2$, therefore

$$C_V \to 0 \quad \text{when} \quad T \to 0$$

(b) At a high temperature $(E/k_BT) \ll 1$, and equation (2) reduces to

$$C_V = k\left(\frac{E}{k_BT}\right)^2 \frac{1}{4}$$

Hence,

$$C_V \to 0 \quad \text{when} \quad T \to \infty$$

Two Level System

In a system of N independent particles, each particle can have only one of the two energies, $-\in$ and $\in$. Suppose N_1 particles are in the state with energy $-\in$ and N_2 in the state with energy $\in$, total energy of the system is $E = M\in = -N_1\in + N_2\in$ so that $M = N_2 - N_1$. Since $N = N_2 + N_1$, we have

$$N_1 = \frac{1}{2}(N - M) \quad N_2 = \frac{1}{2}(N + M)$$

There are $N!/(N_1!\, N_2!)$ possibly ways of choosing N_1 particles out of N to occupy the state $-\in$ and of them gives a different microscopic state energy E. Hence the thermodynamics weight is

$$W_i = {}^{N}C_{N_1} \frac{N!}{\left[\frac{1}{2}(N-M)\right]!\left[\frac{1}{2}(N+M)\right]!}$$

The entropy of the system is

$$S = k_B\, \ell n\, W_i$$

$$= k_B\left[N\ \ell n\ N - \frac{1}{2}(N-M)\,\ell n\frac{1}{2}(N-M) - \frac{1}{2}(N+M)\,\ell n\frac{1}{2}(N+M)\right]$$

$$= -k_B\left[N_1\ \ell n(N_1/N) + N_2\ \ell n(N_2/N)\right]$$

Here, we used Stirling's approximation formula i.e.

$$\ell nN! = N\ell nN - N \qquad \text{(for large } N\text{)}$$

The temperature T is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{\partial S}{\partial M}\frac{\partial M}{\partial E} = \frac{1}{\in}\frac{\partial S}{\partial M} = \frac{k}{2\in}\ell n\left(\frac{N-M}{N+M}\right)$$

This equation shows that $T<0$ for $M>0$ $(E>0)$. This case is unacceptable on the physical ground. However, the system is normal in the range $M<0$ $(E<0)$ and we can discuss the properties of this system of this case. From this equation, we have

$$\frac{N_1}{N_2} = \frac{N-M}{N+M} = \exp(2\in/kT)$$

or

$$\frac{N_1}{N} = \frac{\exp(\in/kT)}{\exp(\in/kT) + \exp(-\in/kT)}$$

$$\frac{N_2}{N} = \frac{\exp(-\in/kT)}{\exp(\in/kT) + \exp(-\in/kT)}$$

These relations give the probabilities of finding any one particle in the states $-\in$ and $\in$ respectively. The energy

$$E = N_2\in - N_1\in = -N\in \tanh(\in/k_BT)$$

The specific heat at constant volume C_V is

$$C_V = \left[\frac{\partial E}{\partial T}\right]_V = N\,k\,(\in/kT)^2\ \text{sech}^2(\in/k_BT)$$

Magnetic System

A system comprising N identical particles is placed in a uniform magnetic field H and is kept at a temperature T. When a particle having spin 1/2 is placed in a magnetic field H, its each energy level splits into two with changes in energies by $-\mu H$ and μH and the particle has a magnetic moment μ or $-\mu$ along the direction of the magnetic field, respectively.

As the spins of particles are independent of each other, the partition function of the total system Z_N is equal to the product of the partition functions for spins of individual particle. The partition function for spins of individual particle is

$$Z_1 = e^{\mu H/k_B T} + e^{-\mu H/k_B T} = 2\cosh(\mu H/k_B T)$$

Thus,

$$Z_N = Z_1^N = \left[2\cosh(\mu H/k_B T)\right]^N$$

The Helmholtz free energy is

$$F = -k_B T \ \ell n\, Z_N = -Nk_B T \ \ell n\left[2\cosh(\mu H/k_B T)\right]$$

The entropy is

$$S = -\frac{\partial F}{\partial T} = Nk_B\left[\ell n\{2\cosh(\mu H/k_B T)\} - (\mu H/k_B T)\tanh(\mu H/k_B T)\right]$$

Total energy is $U = F + TS = -N\mu H \tanh(\mu H/k_B T)$

Total magnetic moment is

$$M = -\frac{\partial F}{\partial H} = N\mu \tanh(\mu H/k_B T)$$

The specific heat at constant volume C_V is

$$C_V = \left[\frac{\partial U}{\partial T}\right]_H = Nk_B(\mu H/k_B T)^2 \operatorname{sech}^2(\mu H/k_B T)$$

Problem: Consider a system of N non-interacting spins, each of which has classical magnetic moment of magnitude μ. The Hamiltonian of this system in an external magnetic field $\vec{H}$ is $H = -\sum_{i=1}^{N} \vec{\mu}_i.\vec{H}$, where $\vec{\mu}_i$ is the magnetic moment of the i^{th} spin. The magnetization per spin at temperature T is:

(a) $\dfrac{\mu^2 H}{k_B T}$

(b) $\mu\left[\coth\left(\dfrac{\mu H}{k_B T}\right) - \dfrac{k_B T}{\mu H}\right]$

(c) $\mu \sinh\left(\dfrac{\mu H}{k_B T}\right)$

(d) $\mu \tanh\left(\dfrac{\mu H}{k_B T}\right)$

Soln. Interaction energy $= -\vec{\mu}.\vec{H}$

$$\langle \mu_z \rangle = \frac{\int \mu_z e^{+\vec{\mu}.\vec{H}/k_B T} d\Omega}{\int e^{+\vec{\mu}.\vec{H}/k_B T} d\Omega}$$

$$\langle \mu_z \rangle = \frac{\mu \int_0^{2\pi}\int_0^{\pi} \cos\theta e^{\mu H\cos\theta/k_B T} \sin\theta d\theta d\varphi}{\int_0^{2\pi}\int_0^{\pi} e^{\mu H\cos\theta/k_B T} \sin\theta d\theta d\varphi}$$

[Using $\int d\varphi = 2\pi$ and *put* $\cos\theta = x$, $\mu H/k_B T = a$]

$$\langle \mu_z \rangle = \frac{\mu \int_0^{\pi} \cos\theta \, e^{a\cos\theta} \sin\theta d\theta}{\int_0^{\pi} e^{a\cos\theta} \sin\theta d\theta} = \mu \left[\int_{-1}^{+1} x e^{ax} dx \Big/ \int_{-1}^{+1} e^{ax} dx \right]$$

$$\text{First integral} = \mu \left[x \frac{e^{ax}}{a} \Big|_{-1}^{+1} - \frac{1}{a} \int_{-1}^{1} e^{ax} dx \right] = \mu \left[\left(\frac{e^{a} + e^{-a}}{2a} \right) - \frac{1}{a} \left| \frac{e^{ax}}{a} \right|_{-1}^{+1} \right]$$

$$= \mu \left[\frac{2\cosh a}{a} - \frac{1}{a^2} \sinh a \right] = \frac{2\mu}{a} \left[\cosh a - \frac{\sinh a}{a} \right]$$

$$\text{Second integral} = \int_{-1}^{+1} e^{ax} dx = \frac{2\sinh a}{a}$$

$$\langle \mu_z \rangle = \frac{\mu \frac{2}{a} \left(\cosh a - \frac{1}{a} \sinh a \right)}{\frac{2}{a} \sinh a} = \mu \left(\coth a - \frac{1}{a} \right)$$

$$\langle \mu_z \rangle = \mu \left(\coth \frac{\mu H}{kT} - \frac{k_B T}{\mu H} \right)$$

Correct answer is (b)

Problem: Consider a system whose three energy levels are given by 0, ε and 2ε. The energy level ε is two-fold degenerate and the other two are non-degenerate. The partition function of the system with $\beta = \frac{1}{k_B T}$ is given by

(a) $1 + 2e^{-\beta\epsilon}$ (b) $2e^{-\beta\epsilon} + e^{-2\beta\epsilon}$ (c) $\left(1 + e^{-\beta\epsilon}\right)^2$ (d) $1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$

Soln. For the given energy levels the partition function can be written as

$z = e^{-\beta \cdot 0} + 2e^{-\beta\varepsilon} + e^{-\beta \cdot 2\varepsilon}$; where the factor 2 is due to two fold degeneracy of energy level ε.

Therefore, $z = 1 + 2e^{-\beta\varepsilon} + (e^{-\beta\varepsilon})^2 = (1 + e^{-\beta\varepsilon})^2$

Hence correct option is (c).

Problem: Common Data for next two problems

There are four energy levels E, $2E$, $3E$ and $4E$ (where $E > 0$). The canonical partition function of two particles is, if these particles are

(i) Two identical fermions

(a) $e^{-2\beta E} + e^{-4\beta E} + e^{-6\beta E} + e^{-8\beta E}$

(b) $e^{-3\beta E} + e^{-4\beta E} + 2e^{-5\beta E} + e^{-6\beta E} + e^{-7\beta E}$

(c) $(e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + e^{-4\beta E})^2$

(d) $e^{-2\beta E} - e^{-4\beta E} + e^{-6\beta E} - e^{-8\beta E}$

Soln. For fermions the distribution of particles can be as illustrated below.

Energy Level → / Configuration ↓	E	$2E$	$3E$	$4E$
I	A	A		
II	A		A	
III	A			A
IV		A	A	
V		A		A
VI			A	A

From the above table it is clear that :-
Number of configuration with total energy $3E = 1$.
Number of configuration with total energy $4E = 1$.
Number of configuration with total energy $5E = 2$.
Number of configuration with total energy $6E = 1$.
Number of configuration with total energy $7E = 1$.
Hence correct option is (b).

(ii) Two distinguishable particles

(a) $e^{-2\beta E} + e^{-4\beta E} + e^{-6\beta E} + e^{-8\beta E}$ (b) $e^{-3\beta E} + e^{-4\beta E} + 2e^{-5\beta E} + e^{-6\beta E} + e^{-7\beta E}$

(c) $(e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + e^{-4\beta E})^2$ (d) $e^{-2\beta E} - e^{-4\beta E} + e^{-6\beta E} - e^{-8\beta E}$

Soln. Since the particles are indistinguishable they can be treated classically i.e., any number of particles can be present in any level.
Now, the partition function for one particle with the given energy levels can be written as
$Z = e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + e^{-4\beta E}$.
Therefore, the partition function for two particles equal to Z^2.
Hence correct option is (c).

Classical and Quantum Statistics

The study of statistical mechanics can be divided into two main classes :
1. Classical Statistics or Maxwell-Boltzmann Statistics.
2. Quantum Statistics (Fermi-Dirac and Bose-Einstein Statistics)

(1) Classical Statistics

Let there be total N particles out of which n_i particles are in ε_ith energy level having g_i states (or having degeneracy g_i). Let us label the g_i cells. The first particle may occupy any of the g_i cells. The second particle may occupy any of the re-meaning $(g_i - 1)$ cells etc. Thus, the total number of ways of accommodating all n_i particles in g_i cells is $g_i^{n_i}$.
Taking into account for the fact that there are n_i particles in g_i cells for each $i = 1, 2, 3, \ldots$. The total number of ways is $\prod_i g_i^{n_i}$. The total number of particles is N. So, preventing all the particles in which n_i are alike ($i = 1$, 2, 3,...) is $\frac{N!}{\prod n_i!}$.
So, the total number of microstates is

$$\Omega = \frac{N!}{\prod n_i!} \prod_i g_i^{n_i} \qquad \ldots(1)$$

Having found the number of microstates, we are ready to find the most probable state. We maximise $\ell n\, \Omega$ subject to the two constraints

$$\sum_i n_i = N \quad ...(2)$$

$$\sum_i n_i \varepsilon_i = E \quad ...(3)$$

where, N and E are constants.

That gives $\boxed{n_i = g_i e^{-(\beta\varepsilon_i - \alpha)}}$, here $\alpha = -\frac{\mu}{k_B T} = -\frac{E_F}{k_B T}$ and $\beta = \frac{1}{k_B T}$ and g_i is degeneracy factor which is the classical or Maxwell Boltzmann distribution.

(2) Quantum Statistics

• Bose-Einstein Statistics

This statistics is obeyed by identical, indistinguishable particles of integral spin (bosons) that have symmetrical wave function and is so named as it was derived by Bose for light quanta and generalized by Einstein.

Consider a system having n indistinguishable particles. Let these particles be divided into quantum groups or levels such that there are $n_1, n_2, ..., n_i$ number of particles in group whose approximate constant energies are $\varepsilon_1, \varepsilon_2, ..., \varepsilon_i ....$ respectively. Let g_i be the number of eigen states (i.e. degeneracy of statistical weight) of the i th level (for a non degenerate case $(g_i - 1)$.

For finding Bose-Einstein distribution consider a box divided into g_i sections (or cells) and n_i indistinguishable particles are to be distributed among these sections. The choice that which of the sections will head the sequence can be made in g_i ways. Once this has been done the total number of permutations of n_i particles and the remaining $(g_i = 1)$ sections is $(n_i + g_i - 1)$. Thus, the total number of possible ways in which n_i particles can be distributed in g_i sections is

$$g_i[(n_i + g_i + 1)!] \quad ...(4)$$

Since the particles are indistinguishable the permutations of particles among themselves will not give rise to indistinguishable arrangements. Obviously these are $n_i!$ such permutations, hence expression (4) must be divided by $n_i!$. Further, the distributions which arise by mere permutations of sections among themselves do not produce different states. Obviously there are $g_i!$ such permutations hence expressions must also be divided by $g_i!$

Thus, the required number of ways in which n_i particles are to be distributed among g_i sub-levels of ith quantum group is

$$\frac{[g_i (n_i + g_i - 1)!]}{n_i! g_i!} = \frac{(n_i + g_i - 1)!}{n_i (g_i - 1)!}$$

Similar expressions can be found for various other quantum states. Considering all the available quantum groups, with n_1 particles in first group of energy ε_1, n_2 particles in second group of energy ε_2 and so on, the total number of distinguishable arrangements are given by

$$G = \frac{(n_1 + g_1 - 1)}{n_1!(g_1 - 1)!} \cdot \frac{(n_2 - g_2 - 1)!}{n_2!(g_2 - 1)!} \cdot \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad ...(5)$$

As n_i and g_i are large numbers, we may neglect one in above expression therefore, equation (5) may be written as

$$G = \prod_i \frac{(n_i + g_i)!}{n_i! (g_i)!} \quad ...(6)$$

In accordance with the postulate of equal a priori probability of states, the probability Ω of the system for occuring with the specified distribution is proportional to the total number of eigen states, i.e.,

$$\Omega = \prod_i \frac{(n_i + g_i)!}{n_i!\, g_i!} \times \text{constant} \quad ...(7)$$

$$= C \prod_i \frac{(n_i + g_i)!}{n_i!\, g_i!} \text{ where } C \text{ is constant}$$

The distribution law of Bose-Einstein statistics can now be obtained by determining the most probable distribution as in classical statistics.

That gives $\boxed{n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} - 1}}$

This equation represents the most probable distribution of the particles among various energy levels for a system obeying Bose-Einstein statistics and is therefore known as *Bose-Einstein's distribution law.*

- **Fermi-Dirac Statistics**

This statistics is obeyed by indistinguishable particles of half-integral spin that have anti-symmetric wave functions and obey Pauli exclusion principle.

Consider a system having n indistinguishable particles. Let these particles be divided into quantum groups or levels such that there are $n_1, n_2, ..., n_i ...$ number of particles in groups whose approximate constant energies are $\varepsilon_1, \varepsilon_2, ... \varepsilon_i ...$ respectively. Let g_i denote the degeneracy or statistical weight (i.e., number of sublevels) of ith level.

Since due to Pauli's principle, no cell can occupy more than one particle, therefore among g_i cells only n_i cells are occupied by one particle each and the remaining $(g_i - n_i)$ cells are empty. The possible number of such a distribution is given by $g_i!$ corresponding to the permutations of the g_i cells. But as the particles are indistinguishable, therefore all the occupied n_i cells are similar to each other. Hence $n_i!$ permutations of occupied cells will not give rise to indistinguishable arrangements. Further $(g_i - n_i)!$ permutations of empty cells among themselves also give rise to indistinguishable arrangements. Hence, the number of distinguishable arrangements of n_i particles in g_i cells are

$$\frac{g_i}{n!(g_i - n_i)} \qquad ...(1)$$

Similar expressions can also be found for various other quantum states. Considering all the available quantum groups, with n_i particles in first group of energy ε_1; n_2 particles in second group of energy ε_2 and so on and keeping in mind that due to indistinguishable of particles, the division of total number of n particles into groups of $n_1, n_2, ..., n_i ...$ particles can be done in only one way; the total number of eigen states for the whole system is given by

$$G = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \qquad ...(2)$$

In accordance with the postulate of equal a priori probability of states, the probability Ω of the system for occuring with the specified distribution is proportional to the total number of eigenstates i.e.,

$$\Omega = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \times \text{constant}$$

$$= C \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \qquad ...(3)$$

where, C is a constant.

The Fermi-Dirac distribution law can be obtained by determining the most probable distribution.

The two subsidiary conditions are :

1. The total number of particles of the systems is constant $n = \sum_i n_i = \text{constant}$

or $\delta n = \delta n_i = 0 \qquad ...(4)$

2. Total energy of the system is constant

i.e., $E = \sum n_i \varepsilon_i = \text{constant}$

i.e., $\delta E = \sum_i \varepsilon_i \delta n_i = 0 \qquad ...(5)$

That gives $\boxed{n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} + 1}}$

This equation represents the most probable distribution of the particles among various energy levels for a system obeying Fermi-Dirac statistics and is therefore known as *Fermi-Dirac distribution law.*

Comparison of Three Statistics

The expressions for the most probable distribution in the three statistics are

(i) Maxwell-Boltzmann Statistics $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}} = \frac{g_i}{e^{(\varepsilon_i-\varepsilon_F)/k_BT}}$

(ii) Bose-Einstein Statistics $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}-1} = \frac{g_i}{e^{(\varepsilon_i-\varepsilon_F)/k_BT}-1}$

(iii) Fermi-Dirac Statistics $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}+1} = \frac{g_i}{e^{(\varepsilon_i-\varepsilon_F)/k_BT}+1}$

It is to be note that if g_i/n_i is very large in comparison to unity, we may write

$$\frac{g_i}{n_i} \approx \frac{g_i}{n_i} + 1 \approx \frac{g_i}{n_i} - 1$$

i.e., for large values of g_i/n_i Bose-Einstein and Fermi-Dirac distributions approach the Maxwell-Boltzmann distribution.

Problem: A Maxwell-Boltzmann gas has two particles in the i-th state whose degeneracy is three. Find out the number of independent ways selecting the particles in the state.

Soln. Here, we have $n_i = 2$, $N = 2$ and $g_i = 3$. The number of independent ways W_i of selecting the particles in the i-th state is $W_i = N!\frac{g_i^{n_i}}{n_i!} = 2!\frac{3^2}{2!} = 9$

Denoting the two distinguisable particles by the alphabets A and B, 9 independent ways of arranging the particles in 3 levels of the state are given in the table below:

Ways	Levels		
	1	2	3
1	A B	–	–
2	–	A B	–
3	–	–	A B
4	A	B	–
5	B	A	–
6	A	–	B
7	B	–	A
8	–	A	B
9	–	B	A

Problem: A Fermi-Dirac gas has two particles in the i-th state whose degeneracy is three. Find out the number of independent ways of selecting the particles in the state.

Soln. Here, we have $n_i = 2$ and $g_i = 3$. The number of independent ways W_i of selecting the particles in the level is

$$W_i = \frac{g_i!}{n_i!(g_i-n_i)!} = \frac{3!}{2!(3-2)!} = \frac{3!}{2!1!} = 3$$

Denoting the two indistinguishable particles by the alphabets A and A, 3 independent ways of arranging the particles, obeying Pauli's exclusion principle, in 3 levels of the state are given in the table below:

Ways	Levels		
	1	2	3
1	A	A	–
2	A	–	A
3	–	A	A

Problem: A Bose-Einstein gas has two particles in the i-th state whose degeneracy is three. Find out the number of independent ways of selecting the particles in the state.

Soln. Here, we have $n_i = 2$ and $g_i = 3$. The number of independent ways W_i of selecting the particles in the state is

$$W_i = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} = \frac{(2+3-1)!}{2!\,(3-1)!} = \frac{4!}{2!\,2!} = 6$$

Denoting the two indistinguishable particles by the alphabets A and A, 6 independent ways of arranging the particles in 3 levels of the state are given in the table below:

Ways	Levels		
	1	2	3
1	A A	–	–
2	–	A A	–
3	–	–	A A
4	A	A	–
5	A	–	A
6	–	A	A

Problem: Let N_{MB}, N_{BE}, N_{FD} denote the number of way in which two particles can be distributed in two energy states according to Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac respectively. Then $N_{MB} : N_{BE} : N_{FD}$ is:

(a) 4 : 3 : 1 (b) 4 : 2 : 3 (c) 4 : 3 : 3 (d) 4 : 3 : 2 **[JAM-2014]**

Soln.

MB

E_1	E_2
AB	
	AB
A	B
B	A

$N_{MB} = 4$

BE

E_1	E_2
..	
	..
.	.

$N_{BE} = 3$

FD

E_1	E_2
.	.

$N_{FD} = 1$

So, $N_{MB} : N_{BE} : N_{FD} = 4 : 3 : 1$

Correct option is (a)

Problem: Which of the following atoms cannot exhibit Bose-Einstein condensation, even in principle?

(a) $^{1}H_{1}$ (b) $^{4}He_{2}$ (c) $^{23}Na_{11}$ (d) $^{40}K_{19}$

Soln. To exhibit Bose-Einstein condensation, particle must be a Boson $\Rightarrow$ Integral spin.

Since, all proton, neutron and electron have half integral spin, only those atoms whose $n_p + n_n + n_e$ is even will be a boson.

where

$$\left.\begin{array}{l} n_p = \text{number of proton} \\ n_n = \text{number of neutron} \end{array}\right\} = n_n = \text{number of neutron} = \text{mass number.}$$

n_e = number of electron

For ${}^{1}H_1 : n_n + n_e = 1 + 1 = 2$ (even) (a)

For ${}^{4}He_2 : n_n + n_e = 4 + 2 = 6$ (even) (b)

For ${}^{23}Na_{11} : n_n + n_e = 23 + 11 = 34$ (even) (c)

For ${}^{40}K_{19} : n_n + n_e = 40 + 19 = 59$ (odd) (d)

So, ${}^{40}K_{19}$ cannot exhibit Bose-Einstein condensation.

Hence, the correct option is (d).

Problem: It is necessary to apply quantum statistics to a system of particles, if
(a) there is substantial overlap between the wave functions of the particles
(b) the mean free path of the particles is comparable to the inter-particle separation
(c) the particles have identical mass and charge
(d) the particles are interacting

Soln. The quantum realm begins when de Broglie wavelength of the particles (or associated with the particles) becomes comparable to the size of the particle. Under this condition, the wavelength of the particles starts overlapping.

Hence, the correct option is (a).

Problem: Consider the Fermi-Dirac distribution function f(E) at room temperature (300 K) where E refers to energy. If E_F is the Fermi energy, which of the following is true?
(a) $f(E)$ is a step function
(b) $f(E_F)$ has a value of 1/2
(c) States with $E < E_F$ are filled completely
(d) $f(E)$ is large and tends to infinity as E decreases much below E_F.

Soln. $$f(E) = \frac{1}{\exp[(E - E_F)/kT + 1]}$$

For $E = E_F$,

$$f(E_F) = \frac{1}{\exp[0] + 1} = \frac{1}{2}$$

Hence correct option is (b).

Problem: A photon gas is at thermal equilibrium at temperature T. The mean number of photons in an energy state $\varepsilon = \hbar\omega$ is:

(a) $\exp\left(\frac{\hbar\omega}{k_B T}\right) + 1$ (b) $\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1$ (c) $\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) + 1\right)^{-1}$ (d) $\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^{-1}$

Soln. The mean occupation number or the average number of particles in a state with energy ε is given by

$$\bar{n} = \frac{1}{\exp\left[(\varepsilon - \mu)/k_B T\right] \pm 1}$$

where, '+' sign is for Fermi-Dirac distribution and '–' sign is for Bose-Einstein distribution.
Since, photon is a Boson, we must use '–' sign.
Also for photon $\mu = 0$.

$$\therefore\ \bar{n}_{\text{photon}} = \frac{1}{\exp\left(\dfrac{\varepsilon}{k_B T}\right) - 1} = \left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^{-1} \qquad (\because\ \varepsilon = \hbar\omega)$$

Hence correct option is (d).

Problem: The probability that an energy level ε at a temperature T is unoccupied by a fermion of chemical potential μ is given by

(a) $\dfrac{1}{e^{(\varepsilon-\mu)/k_B T}+1}$ (b) $\dfrac{1}{e^{(\varepsilon-\mu)/k_B T}-1}$ (c) $\dfrac{1}{e^{(\mu-\varepsilon)/k_B T}+1}$ (d) $\dfrac{1}{e^{(\mu-\varepsilon)/k_B T}-1}$

Soln. The distribution function for fermions is given by $f(\varepsilon) = \dfrac{1}{\exp[(\varepsilon-\mu)/k_B T]+1}$.

Also, $f(\varepsilon)$ = probability that an energy level ε at a temperature T is occupied by a fermions of chemical potential μ.

Therefore, probability than an energy level ε at temperature T is unoccupied by a fermions of chemical potential μ is a $1 - f(\varepsilon)$.

($\because$ Probability of unoccupancy = 1 – probability of occupancy)

$$\Rightarrow \text{Required probability} = 1 - f(\varepsilon) = 1 - \frac{1}{\exp[(\varepsilon-\mu)/k_B T]+1}$$

$$= \frac{\exp[(\varepsilon-\mu)/k_B T]+1-1}{\exp[(\varepsilon-\mu)/k_B T]+1} = \frac{\exp[(\varepsilon-\mu)/k_B T]}{\exp[(\varepsilon-\mu)/k_B T]+1}$$

Dividing numerator and denominator by $\exp[(\varepsilon-\mu)/k_B T]$, we get the required

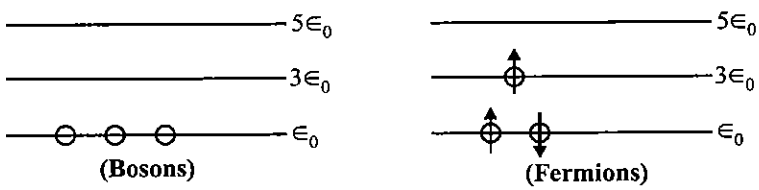
$$\text{probability} = \frac{1}{1+1/\exp[(\varepsilon-\mu)/k_B T]} = \frac{1}{\exp[(\mu-\varepsilon)/k_B T]+1}$$

Hence correct option is (c).

Problem: Consider two different systems each with three identical non-interacting particles. Both have single particle states with energies ε_0, $3\varepsilon_0$ and $5\varepsilon_0$, ($\varepsilon_0 > 0$). One system is populated by spin-$\frac{1}{2}$ fermions and the other by bosons. What is the value of $E_F - E_B$ where E_F and E_B are the ground state energies of the fermionic and bosonic systems respectively?

(a) $6\varepsilon_0$ (b) $2\varepsilon_0$ (c) $4\varepsilon_0$ (d) ε_0

Soln.



According to Pauli's exclusion principle

$E_B = 3\epsilon_0$ $E_F = 2\epsilon_0 + 3\epsilon_0 = 5\epsilon_0$

$E_F - E_B = 5\epsilon_0 - 3\epsilon_0 = 2\epsilon_0$

Correct answer is (b)

Problem: Consider a system of 3 fermions, which can occupy any of the 4 available energy states with equal probability. The entropy of the system is

(a) $k_B \ln 2$ (b) $2k_B \ln 2$ (c) $2k_B \ln 2$ (d) $3k_B \ln 4$

Soln. The distribution of 3 fermions (A, A, A) in 4 energy states (I, II, III, IV) is illustrated in the following table :

States → **Microstates ↓**	1	2	3	4
I	A	A	A	
II	A	A		A
III	A		A	A
IV		A	A	A
Total no. of microstates = 4				

Now, entropy is defined as $S = k_B \ell n \Omega$

where Ω = number of accessible microstates (which is = 4 in present case).

Therefore, $S = k_B \ell n 4 = k_B \ell n 2^2 = 2k_B \ell n 2$.

Hence correct option is (b).

PROBLEMS TO BE PLAYED

1. The probability that an energy level ε at a temperature T is unoccupied by a fermion of chemical potential μ is given by

(a) $\frac{1}{e^{(\varepsilon-\mu)/k_BT}+1}$ (b) $\frac{1}{e^{(\varepsilon-\mu)/k_BT}-1}$ (c) $\frac{1}{e^{(\mu-\varepsilon)/k_BT}+1}$ (d) $\frac{1}{e^{(\mu-\varepsilon)/k_BT}-1}$

2. The density of states between energy ε and $\varepsilon+d\varepsilon$ is

(a) $\frac{4\pi L^2 m}{h^2}d\varepsilon$ (b) $\frac{4\pi L^2 m}{h^2}\frac{1}{\sqrt{\varepsilon}}d\varepsilon$ (c) $\frac{4\pi L^2 m}{h^2}\sqrt{\varepsilon d\varepsilon}$ (d) $\frac{4\pi L^2 m}{h^2}\varepsilon d\varepsilon$

3. The ground state energy E_0 of the system in terms of the Fermi energy E_F and the number of electrons N is given by

(a) $\frac{1}{3}NE_F$ (b) $\frac{1}{2}NE_F$ (c) $\frac{2}{3}NE_F$ (d) $\frac{3}{5}NE_F$

4. Thermodynamic variables of a system can be volume V, pressure P, temperature T, number of particles N, internal energy E and chemical potential μ, etc. For a system to be specified by microcanonical (MC), Canonical (CE) and Grand Canonial (GC) ensembles, the parameters required for the respective ensembles are

(a) $MC:(N,V,T);CE(E,V,N);GC:(V,T,\mu)$

(b) $MC:(E,V,N);CE:(N,V,T);GC:(V,T,\mu)$

(c) $MC:(V,T,\mu);CE:(N,V,T);GC:(E,V,N)$

(d) $MC:(E,V,N);CE:(V,T,\mu);GC:(N,V,T)$

5. Which of the following relations between the particle number density n and temperature T must hold good for a gas consisting of non-interacting particles to be described by quantum statistics?

(a) $n/T^{1/2}<<1$ (b) $n/T^{3/2}<<1$

(c) $n/T^{3/2}>>1$ (d) $n/T^{1/2}$ and $n/T^{3/2}$ can have any value.

6. In a classical micro-canonical ensemble for a system of N non-interacting particles, the fundamental volume in phase space which is regarded as "equivalent to one micro-state" is

(a) h^{3N} (b) h^{2N} (c) h^N (d) h

where h is the Planck's constant.

7. Which of the following statements is true?

(a) In a micro-canonical ensemble the total number of particles N and the energy E are constants while in a canonical ensemble N and temperature T are constants.

(b) In a micro-canonical ensemble the total number of particles N is a constant but the energy E is variable while in a canonical ensemble N and T are constants.

(c) In a macro-canonical ensemble N and E are constants while in a canonical ensemble N and T both vary.

(d) In a micro-canonical ensemble N and E are constants while in a canonical ensemble N is a constant but T varies.

8. A collection of N two-level system with energies 0 and $E>0$ in the thermal equilibrium at temperature T. For $T\to\infty$, the specific heat approaches

(a) 0 (b) Nk_B (c) $3Nk_B/2$ (d) ∞

9. Two particles are said to be distinguishable when

(a) the average distance between them is large compared to their de-Broglie wavelength.

(b) the average distance between them is small compared to their de-Broglie wavelengths.

(c) they have overlapping wavepackets.

(d) their total wave function is symmetric under particle exchange.

10. In a canonical ensemble
(a) the energy and the temperature are constants.
(b) the entropy and the energy are constans.
(c) the temperature and the density are constants.
(d) the density and the entropy are constants.

11. The entropy of a system in the microcanonical ensemble formalism
(a) Is independent of the number of microslates.
(b) Is directly proportional to the number of microstates.
(c) Is inversely proportional to the number of microstates.
(d) Increases logarithmicaly with increase in number of microstates.

12. The difference between Maxwell-Boltzmann (MB), and Bose-Einstein (BE) distribution is that
(a) Both are identical except that one is for classical particles and the other for quantum particles.
(b) Density of occupied states at lower energies is more for BE than for MB.
(c) Density of occupied states at lower energies is less for BE than for MB.
(d) MB is applicable to particles with zero spin and BE to those of finite spin.

13. In a canonical ensemble description of a system, which of the following quantities remain fixed?
(a) Energy of the system
(b) Square of the energy of the system
(c) Volume of the system
(d) Number of particles in the system.

14. The chemical potential μ is:
(a) Positive in Fermi-Dirac statistics (*FD*) and positive in Bose-Einstein statistics (BE) at room temperature (*RT*)
(b) Positive in *FD* and negative in *BE* at *RT*
(c) Negative in Maxwell Boltzmann statistics and negative in *FD* at *RT*.
(d) Always positive in all the three statistics.

ANSWER KEY

1. (c)	**2. (a)**	**3. (b)**	**4. (b)**	**5. (c)**	**6. (a)**	**7. (a)**
8. (a)	**9. (a)**	**10. (c)**	**11. (d)**	**12. (a)**	**13. (c, d)**	**14. (c)**

Appendix-I

Specific & Latent Heats

Specific Heat Capacity

If 'ΔQ' amount of heat absorbed or rejected by a substance of mass 'm' when it undergoes a temperature change 'ΔT', then the specific heat capacity of that substance is given by

$$s = \frac{\Delta Q}{m\,\Delta T} \Rightarrow \Delta Q = ms\,\Delta T$$

It is the property of the substance which determines the change in the temperature of the substance (undergoing no phase change) when a given quantity of heat is absorbed (or rejected) by it.
If the amount of substance is specified in terms of moles 'n' (instead of mass 'm' in kg), we can define molar specific heat capacity (C) as

$$C = \frac{\Delta Q}{\mu \Delta T}$$

- If the gas is held under constant pressure of volume during the heat transfer, then it is called molar specific heat capacity at constant pressure (or volume) and is denoted by C_P (or C_V)
- The specific heat capacity of water is 4186.0 J kg K^{-1} and that of carbon is 506.5 J kg^{-1} K^{-1}. It means that you need eight times more heat to raise the temperature of water by the same amount as that of carbon.

Latent Heat:

It heat is added to a given quantity of ice at –10°C, the temperature of ice increases until it reaches its melting point (0°C). At this temperature, the addition of more heat does not increase the temperature but causes the ice to melt, of change its state. Once the entire ice melts, adding more heat will cause the temperature of the water to rise. A similar situation occurs during liquid gas change of state at the boiling point. Adding more heat to boiling water causes vaporisation, without increase in temperature.
The heat required during a change of state depends upon the heat of transformation and the mass of the substance under going a change of state. Thus, if mass 'm' of a substance under goes a change from one state to the other, then the quantity of heat required is given by

$$Q = mL$$

where L is the latent heat and is a characteristic of the substance. Its SI unit is J/kg. The value of L also depends on the pressure. Its value is usually quoted at standard atmospheric pressure. The latent heat for a solid-liquid state change is called the latent heat of fusion (L_f) and that for a liquid-gas state change is called the latent heat of vaporisation (L_v).

Appendix-II

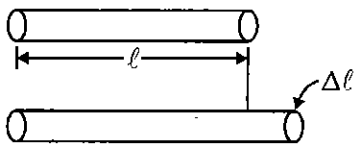
Thermal Expansion

You may have observed that sometimes sealed bottles with metallic lids are so tightly screwed that one has to put the lid in hot water for sometime to open the lid. This would allow the metallic cover to expand, thereby loosening it to unscrew easily. In case of liquids, you may have observed that mercury in a thermometer rises, when the thermometer is put in a slightly warm water. If we take out the thermometer from the water, the level of mercury falls again. Similarly, in the case of gases, a balloon partially inflated in a cool roommay expand to full size when placed in warm water on the other hand, a fully inflated balloon when immersed in cold water would start shrinking due to contraction of the air inside.

It is our common experience that most substances expand on heating and contract on cooling. A change in the temperature of a body causes change in its dimensions. The increase in the dimension of a body due to the increase in its temperature is called *thermal expansion*. The expansion in length is called *linear expansion*. The expansion in area is called *area expansion*. The expansion in volume is called *volume expansion*.

If the substance is in the form of a long rod, then for small change in temperature, ΔT, the fractional change in length, $\Delta \ell / \ell$, is directly proportional to ΔT.

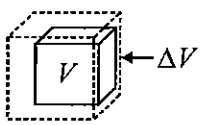
$$\Rightarrow \quad \boxed{\frac{\Delta \ell}{\ell} = \alpha_\ell \, \Delta T} \qquad \ldots (1)$$



where α_ℓ is known as the *coefficient of linear expansion* and is characteristic of the material. The values of α_ℓ for copper and glass are $1.7 \times 10^{-5}\,K^{-1}$ and $0.32 \times 10^{-5}\,K^{-1}$. It means that copper expands about five time more than glass for the same rise in temperature. Normally, metals expand more and have relatively high values of α_ℓ.

Similarly, we consider the fractional change in volume, $\Delta V/V$, of a substance for temperature ΔT and define the coefficient of volume expansion α_V, we have then

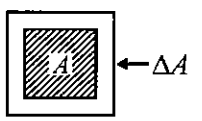
$$\boxed{\frac{\Delta V}{V} = \alpha_V \, \Delta T} \qquad \ldots (2)$$



where α_V is also characteristic of the temperature.

Similarly, for area expansion, we have

$$\boxed{\frac{\Delta A}{A} = \alpha_A \, \Delta T} \qquad \ldots (3)$$



Relation between α_ℓ, α_A and α_V

Imagine a cube of length ℓ, that expands equally in all directions, when its temperature increases by ΔT, we have

$$\Delta \ell = \alpha_\ell \ell \Delta T \qquad \ldots (4)$$

So change in the volume of the cube,

$$\Delta V = (\ell + \Delta \ell)^3 - \ell^3 = 3\ell^2 \Delta \ell \qquad \ldots (5)$$

where we have neglected terms in $(\Delta \ell)^2$ and $(\Delta \ell)^3$ as they are small compared to ℓ.

So, $\Delta V = \frac{3V}{\ell} \Delta \ell = 3V \alpha_\ell \Delta T$ ... (6) [Using (4)]

Also by definition, $\Delta V = \alpha_V V \Delta T$ ... (7)

From equations (6) and (7), $\alpha_V = 3\alpha_\ell$ ... (8)

Similarly, we have can obtain, $\boxed{\frac{\alpha_V}{3} = \frac{\alpha_A}{2} = \alpha_\ell}$ ... (9)

Problem: An aluminium flagpole is 33m high. By how much does its length increase as the temperature increases, by 15°C?

(The coefficient of linear expansion for aluminium is $2.5 \times 10^{-5} K^{-1}$).

(a) 1.24 mm (b) 12.4 mm (c) 1.24 cm (d) 12.4 cm

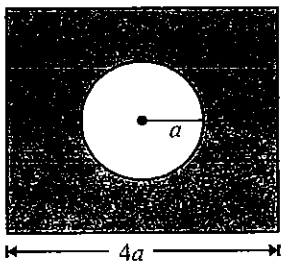
Soln. Given $\ell = 33m$; $\Delta T = 15°C = 15K$; $\alpha_\ell = 2.5 \times 10^{-5} K$

Using, $\frac{\Delta \ell}{\ell} = \alpha_\ell \Delta T$

$\Rightarrow \quad \Delta \ell = \alpha_\ell \Delta T \cdot \ell = 2.5 \times 10^{-5} \times 15 \times 33 = 1.24$ cm

Correct option is (c)

Problem: A thin square sheet of copper (coefficient of linear expansion α) of side $4a$ has a circular hole of radius a cut out symmetrically as shown below :



If the temperature of the sheet is increased by an amount ΔT, the area of the sheet changes by

(a) $(16+\pi)\alpha a^2 \Delta T$ (b) $2(16+\pi)\alpha a^2 \Delta T$ (c) $(16-\pi)\alpha a^2 \Delta T$ (d) $2(16-\pi)\alpha a^2 \Delta T$

Soln. The area of the plate is

$$A = (4a)^2 - \pi(a)^2 = (16-\pi)a^2$$

The coefficient of area expansion, $\alpha_A = 2\alpha$

So the change in area is

$$\Delta_A = \alpha_A A \Delta T$$

$$\Rightarrow \quad \Delta A = 2\alpha(16-\pi)a^2 \Delta T$$

$\Rightarrow \quad \Delta A = 2(16-\pi)\alpha a^2 \Delta T$

Correct option is (d)

Problem: The coefficient of volume expansion of glycerin is $49\times10^{-5}\ K^{-1}$. What is the fractional change in its density for a 30°C rise in temperature?

(a) 1.5×10^{-2} (b) 1.5×10^{-3} (c) 0.15×10^{-2} (d) 0.15×10^{-3}

Soln. Given: $\alpha_v = 49\times10^{-5}K^{-1}$; $\Delta T = 30°C = 30K$

The density is defined as

$$d = \frac{m}{V}$$

where m is the mass and V is the volume

$$\Rightarrow \quad \Delta d = \frac{-m}{V^2}\Delta V$$

$$\therefore \quad \left|\frac{\Delta d}{d}\right| = \left|-\frac{\Delta V}{V}\right| = \alpha_v \Delta T$$

$$= 49\times10^{-5}\times30 = 0.14770 = 1.5\times10^{-2}$$

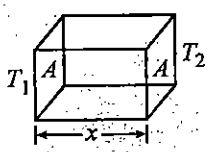
Correct option is (a)

CAREER ENDEAVOUR

Appendix-III

Thermal Conduction

If one end of a metal rod is placed in a store, the temperature of the rod gradually increases. Heat starts transfering from one end to the another end of the rod. This process of transfering of heat is called heat conduction and the molecular collisions are responsible for it. Some materials easily transmits the heat from end to the other but some takes a very large amount of time to do so. This ability of a material to conduct heat is measured by "thermal conductivity" of the material.



Consider a slab of uniform cross-section A and length x. Let one face of the slab be at temperature T_1 and the other at T_2. In order to avoid the transfer of heat from the sides, we have covered the remaining surfaces with a non-conducting material.

After sufficient time, steady state is reached and the temperature remains unchanged as the time passes. It is found that in steady state the heat current $(\Delta Q/\Delta t)$ is proportional to the temperature difference $(T_1 - T_2)$ between the ends, proportional to the area of cross-section and inversely proportional to the length x.

Mathematically, $\frac{\Delta Q}{\Delta t} = \frac{K A (T_1 - T_2)}{x}$

CAREER ENDEAVOUR

where K is a constant for the material of the slab and is called the *thermal conductivity* of the material.

If the area of the cross-section is not uniform or if the steady state condition is not reached the equation can only be applied to a thin layer of material perpendicular to heat flow. If dT be the temperature difference along the layer of thickness dx, the heat current is given by

$$\frac{dQ}{dt} = -KA\frac{dT}{dx}$$

where the quantity dT/dx is called the *temperature gradient*. The minus sign indicates that dT/dx is negative along the direction of the heat flow.

The unit of thermal conductivity is J $s^{-1}m^{-1}$ K^{-1} or J $s^{-1}m^{-1}$ $°C^{-1}$ or W m^{-1} K^{-1} or W m^{-1} $°C^{-1}$.

Problem : One face of a copper cube of edge 10 cm is maintained at 100 °C and the opposite face is maintained at 0°C. All other surfaces are covered with an insulating material. Find the amount of heat flowing per second through the cube. (Thermal conductivity of copper is 385 W m^{-1} $°C^{-1}$).

Soln. The amount of heat flowing per second is :

$$\frac{\Delta Q}{\Delta t} = \frac{KA(T_1 - T_2)}{x} = \frac{385 \times (10\text{ cm})^2 \times (100 - 0)\,°\text{C}}{(10\text{ cm})}$$

$$= 3850\text{ W}.$$

Problem : Two bars, both if length ℓ and cross sectional area A, made of different materials with thermal conductivities K_1 and K_2 are joined together to form a composite bar of length 2ℓ. The free ends of the composite bar are kept at temperatures T_1 and T_2. The temperature at the junction of the two bars is:

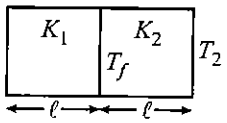
(a) $\dfrac{\ell^2(T_1+T_2)\sqrt{K_1K_2}}{2A(K_1+K_2)}$ (b) $\dfrac{T_1T_2(K_1+K_2)}{(T_1+T_2)\sqrt{K_1K_2}}$

(c) $\dfrac{K_1T_1+K_2T_2}{K_1+K_2}$ (d) $\dfrac{T_1+T_2}{2}$

Soln. Let the final temperature of the junction be T_f. Then,

Since, ends are joined together to form a composite bar, the heat current is same in both the bars. So, we have

$$\left(\frac{\Delta Q}{\Delta t}\right)_1 = -\left(\frac{\Delta Q}{\Delta t}\right)_2$$ [The minus sign indicates the exchange of heat]



$$\Rightarrow \quad \frac{K_1A(T_f-T_1)}{\ell} = -\frac{K_2A(T_f-T_2)}{\ell}$$

$$\Rightarrow \quad K_1(T_f-T_1) = -K_2(T_f-T_2)$$

$$\Rightarrow \quad T_f = \frac{K_1T_1+K_2T_2}{K_1+K_2}$$

Correct option is (c).

Problem : If a metal rod is heated at one end and immersed in ice (at 0°C) at the other end, then the mass of ice that melts in a given time, t, is

(a) directly proportional to the length of the rod and inversely proportional to the area of cross-section.
(b) directly proportional to the area of cross-section and inversely proportional to thermal conductivity of the rod.
(c) directly proportional to both the length and thermal conductivity of the rod. **[H.C.U.-2012]**
(d) directly proportional to the thermal conductivity of the rod and inversely proportional to its length.

oln. The heat current is given by

$$\frac{\Delta Q}{\Delta t} = \frac{KA(T_1-T_2)}{x}$$

where $\Delta Q = mL_f$ (as ice is melting)

Since, $\dfrac{mL_f}{\Delta t} = \dfrac{KA(T_1-T_2)}{x}$

$$\Rightarrow \quad m = \frac{KA(T_1-T_2)}{x}\frac{\Delta t}{L_f}$$

Clearly, $m \propto K$ and $m \propto \dfrac{1}{x}$.

Correct option is (d).

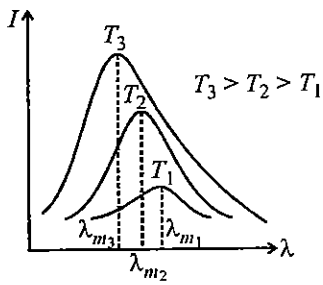
Appendix-IV

Blackbody Radiation

A body that absorbs all the radiation falling on it is called a *blackbody*. Such a body will emit radiation at the fastest rate. The radiation emitted by a blackbody is called *blackbody radiation*. A blackbody is also called an ideal radiator. Among the materials, lampblack is close to a blackbody. If reflects only about 1 % of the radiation falling on it.

Wiens's Displacement Law

The intensity of thermal radiation emitted by a body (not necessarily a blackbody) near a given wavelength is plotted against the wavelength for different temperatures. We see that as the temperature is increased, the wavelength corresponding to the highest intensity decreases. In fact, this wavelength λ_m is inversely proportional to the absolute temperature of the emitter. So, $\lambda m T = b$, where b is a constant known as Wien's constant and is equals to 2.8979×10^{-3} m·K for a blackbody.



Problem : The light from the Sun is found to have a maximum intensity near the wavelength of 470 nm. Assuming that the surface of the Sun emits as a blackbody, calculate the temperature of the surface of the Sun.

Soln. For a blackbody, $\lambda m T = 2.8979 \times 10^{-9}\ m \cdot K$

Thus, $T = \dfrac{2.8979 \times 10^{-3}\ m \cdot K}{470 \times 10^{-9}\ m} \simeq 6165\ K$

Problem : The intensity of radiation emitted by the Sun has its maximum value at a wavelength of 500 nm. The corresponding value for the value the star Polaris is 380 nm. Assuming that these stars behave like blackbodies, the ratio (T_S / T_P) of the surface temperature of the Sun Polaris is **[JNU 2011]**

(a) 1.70 (b) 1.32 (c) 0.76 (d) 0.58

Soln. Given $(\lambda m)_s = 500$ nm ; $(\lambda m)_p = 380$ nm

For a blackbody, $\lambda m T = 2.8979 \times 10^{-3}\ m \cdot K$

$$\Rightarrow \frac{T_s}{T_p} = \frac{(\lambda m)_p}{(\lambda m)_s} = \frac{380}{500} \simeq 0.76$$

Correct option is (c).

Stefan-Boltzmann Law

The energy of thermal radiation emitted per unit time by a body of surface area A and temperature T is given by

$$u = e\sigma AT^4$$

where σ is called the Stefan-Boltzmann's constant and is equals to $5.67 \times 10^{-8}\ \text{W m}^{-2}\text{K}^{-4}$. Also, the e is called *emissivity* of the surface and its value lies between 0 and 1. It is equal to unity for blackbodies.

Problem : A blackbody of surface area 10 cm^2 is heated to 127 °C and is suspended in a room at temperature 27 °C. Calculate the initial rate of loss of heat from the body to the room.

Soln. For a blackbody at temperature T, the rate of emission is $u = \sigma AT^4$

When it is kept in a room at temperature to, the rate of absorption is $u_0 = \sigma AT_0^4$.

Therefore, the net rate of loss of heat is $u - u_0 = \sigma A(T^4 - T_0^4)$.

Here, $A = 10 \times 10^{-4} m^2$, $T = 400\,K$, $T_0 = 300\,K$

Therefore, $u - u_0 = (5.67 \times 10^{-8})\,(10 \times 10^{-4})\,(400^4 - 300^4) = 0.99\,W$

Problem : The power per unit area emitted by a surface of a blackbody (in Wm^{-2}) at temperature 230 K is about

(a) 112.67 (b)128.67 (c) 158.67 (d) 178.67 **[DU 2016]**

Soln. The power emitted by a blackbody is

$P = \sigma AT^4$; $\sigma = 5.67 \times 10^{-8}\ \text{W m}^{-2}\text{K}^{-4}$

So, power per unit area is

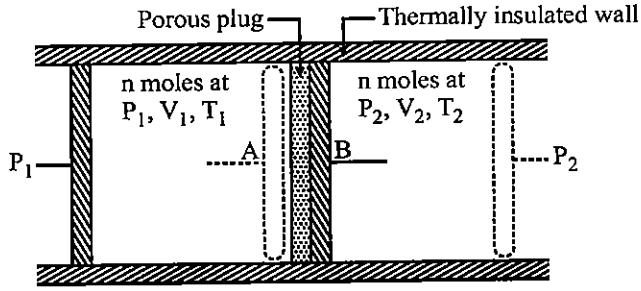
$$\frac{P}{A} = \sigma T^4 = 5.67 \times 10^{-8} \times 230^4 = 158.67\ \text{W m}^{-2}.$$

Correct option is (c).

Appendix-V

Joule-Thomson Experiment

In 1852, Lord Kelvin Thomson in collaboration with Joule devised an experiment, usually known as the *porous plug experiment*. In this experiment, a highly compressed gas is being continuously forced at constant pressure through a porous plug. The gas during its passage through the pores becomes throttled or wire drawn, viz., the molecules of the gas are drawn further apart from the one another. The gas thus suffers a volume expansion.



(*The dotted lines indicate the final position of the piston*)

The apparatus used by Joule and Thomson is shown in the above figure. A continuous flow of gas at a much higher pressure P_1 and higher temperature T_1 is forced through a porous plug in a tube, from which it emerges at a lower pressure P_2 and a lower temperature T_2, since the plug offers great resistance to the flow of the gas. The plug is surrounded by a non-conducting jacket so that the process is adiabatic. Therefore, this process is known as *Joule-Thomson Expansion* or *Adiabatic Throttling*.

Theory of Joule-Thomson experiment

Suppose that the pressure on the two sides of the porous plug are kept constant at values P_1 and P_2, where $P_2 < P_1$. Let us assume that before the process starts the gas on one side has internal energy U_1. After expanding through porous plug let the internal energy of the gas on other side be U_2. If the piston A (shown in figure) is slowly moved towards plug so as to keep the pressure constant at P_1 as the gas escapes, then the piston B will move slowly outward to keep the pressure on the other side constant at P_2. If x_1 and x_2 be the distances through which the piston A and B move respectively and 'a' the area cross-section of the piston, then

The force acting at piston $A = P_1 a$

So, work done by this force upon the gas is $P_1 a x_1 = P_1 V_1$.

Similarly, the work done by the gas in forcing the piston $B = P_2 a x_2 = P_2 V_2$.

Therefore, the net workdone by the gas is $W = P_2 V_2 - P_1 V_1$.

Since, the device is thermally insulated $dQ = 0$, and from the first law of thermodynamics, the work done by the system is equal to the decrease in its internal energy, $U_1 - U_2$,

i.e., $P_2 V_2 - P_1 V_1 = U_1 - U_2$ or $U_1 + P_1 V_1 = U_2 + P_2 V_2$ or $H_1 = H_2$.

Hence, the enthalpy change in the throttling process, i.e., $dH = 0$.

Thus, we conclude that the enthalpy is conserved. So, in the throttling process, enthalpy remains constant. This process is known as Joule Thomson or Joule Kelvin expansion which is '*quasistatic isenthalpic*' in nature.

Joule-Thomson Coefficient

Joule-Thomson coefficient (μ) is the ratio of changes in temperature to the change in pressure at constant enthalpy and calculated to be equal to

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \qquad \ldots (1)$$

For Ideal Gas, $\mu = 0$.

The Joule Thomson coefficient is zero means there is no change in temperature of a perfect gas, if it is expand adiabatically across the porous plug.

For van der Waals' gas,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \qquad \ldots (2)$$

As the pressure is lower on the emergent side of the porous plug therefore, the dP is necessarily a negative quantity.

Estimates of Joule-Thomson Cooling

It is clear from the equation (2) that for a given difference in pressure on two sides of plug,

1. If $T < \frac{2a}{Rb}$ then right side term would be positive, hence dT will be negative or the gas will be cooled down on passing through porous plug.
2. If $T > \frac{2a}{Rb}$, then right side term would be negative, hence dT will be positive or the gas will be heated up on passing through porous plug.
3. If $T = \frac{2a}{Rb}$, then right side term would be zero, hence dT will be zero or the gas will be neither cooled nor warmed on passing through porous plug, i.e., no change in temperature.

The temperature below which the gases shows cooling effect and above which shows heating effect is known as the *temperature of inversion*, and is written as

This shows that Joule-Thomson expansion will necessarily cool a gas if its initial temperature is below its inversion temperature.

Problem: Calculate the drop in temperature produced by adiabatic throttling process in the case of oxygen when the pressure is reduced by 40 atmospheres. Initial temperature of the gas obeys van der Waals' equation. The values of few constants are given as,

$a = 1.3 \times 10^{12}$ cm^4 dynes/mole^2, $b = 31.2$ cm^3/mole, $C_p = 7$ cal/mole-K

Soln. Using equation (2), $\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$ or $\partial T = \frac{\partial P}{C_p}\left[\frac{2a}{RT} - b\right]$

$\partial P = 40$ atmosphere $= 40 \times 76 \times 13.6980$ dynes/cm^2

$$C_p = 7\frac{\text{cal}}{\text{mole-K}} = \frac{7 \times 4.2 \times 10^7 \text{ ergs}}{\text{mole-K}}; \; T = 30\,^\circ\text{C} = 303\text{ K}; \; R = \frac{8.32 \times 10^7 \text{ ergs}}{\text{mole-K}}$$

$$\text{So, } \partial T = \left[\frac{40 \times 76 \times 13.6 \times 980}{7 \times 4.2 \times 10^7}\right]\left[\frac{2 \times 1.32 \times 10^{12}}{9.31 \times 10^7 \times 303} - 31.2\right]$$

$$= 10.16\,^\circ\text{C} = 10.16\text{ K}.$$